ORGANOMETALLIC COMPLEXES AS LIGANDS

by

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DECLARATION

This thesis consists of original work carried out by the author at the Chemistry Department, Glasgow University, and at Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, Runcorn, Cheshire.

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A paper on the complexes $Cp_2Ti\left[SR\right]_2M'(CO)_4$, as described in Chapter 2, Section 2, has been accepted for publication in the Journal of the Chemical Society.

Two papers, one on the complexes $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, as described in Chapter 2 Section 3, and the other on the complexes $(Cp_2Ti\left[SR\right]_2CuX)_n$, Chapter 3, have been submitted for publication in the Journal of the Chemical Society.

SUMMARY

Complexes which contain two or more transition metals have been prepared and characterised. The preparations have, in the main, been carried out using ligand replacement reactions leading to complexes which contain two transition metals linked together by two bridging ligands.

Spectroscopic evidence suggests that some of the complexes contain metal-metal bonds whereas others do not. The metal-metal bond in these complexes is unusual in that it is a dative bond formed by two electrons which formally belong to only one of the metals.

The complexes which have been prepared and studied are as follows:- bis-π-cyclopentadienyl titanium di-μ-organothio tetracarbonyls of Group VI, $Cp_2Ti\left[SR\right]_2M'(CO)_4$, I, (R= Me,Ph; M' = Cr,Mo,W); chelating diphosphine or diarsine palladium^{II} or platinum^{II} di-μ-organothio tetracarbonyls of Group VI, $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, II, (L-L= 1,2 bis-diphenylphosphino ethane, o-phenylene bis-diethylarsine; M = Pd,Pt; R = Me,Ph; M' = Cr,Mo,W);

bis-π-cyclopentadienyl titanium di-μ-organothio cuprous halides, $(Cp_2Ti\left[SR\right]_2CuX)_n$, IV, (R = Me, Ph; X = Cl, Br); 1,2 bis-diphenylphosphino ethane palladium^{II} or platinum^{II} di-μ-methylthio palladium dichlorides, $Ph_2PCH_2CH_2PPh_2M\left[SMe\right]_2PdCl_2$, VI, (M = Pd, Pt); and 1,2 bis-diphenylphosphino ethane palladium^{II} di-μ-chloro palladium dichloride, $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$, VII.

In order to examine the properties of the above complexes, it has been necessary to prepare and study the "parent" complexes $RSCH_2CH_2SRM'(CO)_4$, III, (R = Me, Ph; M' = Cr, Mo, W); $(RSCH_2CH_2SRCuX)_n$, V, (R = Me, Ph; X = Cl, Br); $Cp_2Ti(SR)_2$, (R = Me, Ph); and $(L\text{-}L)M(SR)_2$, (L-L = 1,2 bis-diphenylphosphino ethane, o-phenylene bis-diethyl arsine; M = Pd, Pt; R = Me, Ph).

Because of the different physical properties, especially solubility, of the complexes prepared, it has been found necessary to use different techniques to examine their chemical properties. The molecular structure of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$, together with infra-red, ^{1}Hn.m.r., and electronic data suggest that complexes I contain a metal-metal bond. There is evidence for a metal-metal bond in complexes IV, from their electronic spectra. The infra-red (4,000-400cm.$^{-1}$), far infra-red (400-40cm.$^{-1}$), and electronic spectra of complexes II, VI, and VII show no evidence of a metal-metal bond.

Tentative correlations have been made between the metal-bridge stretching frequencies and the strengths of the metal-bridge bonds.

The failure to prepare (by nucleophilic displacement or elimination reactions) complexes containing two transition metals bridged by silicon or titanium, and the unusual products obtained from some of the ligand replacement reactions are assigned to lability or over-stability of the reaction intermediates or lability of the desired products.

INTRODUCTION

Multi-heteronuclear complexes containing transition metals have been known for several years. There are 2 classes of such complexes: those which contain both transition and main group metals, and those which contain only transition metals. The majority of the heteronuclear complexes are those in which a main group metal, especially a Group IV metal, or a post transition metal is bonded to a transition metal, but there is an ever-increasing number of complexes containing only transition metals.

The main types of reactions which have been used to prepare complexes containing both transition and main group metals are listed below:-

1). Nucleophilic displacement reactions.

a) $H_3SiI + NaCo(CO)_4 \longrightarrow H_3SiCo(CO)_4 + NaI$ [1].

b) $InBr_3 + 3NaCo(CO)_4 \longrightarrow In(Co(CO)_4)_3 + 3NaBr$ [2].

c) $Cp_2ZrCl_2 + Ph_3SiLi \longrightarrow Cp_2Zr(Cl)SiPh_3 + LiCl$ [3].

d) $(OC)_5MnSnPh_2Cl + NaMoCp(CO)_3 \longrightarrow (OC)_5Mn[SnPh_2]MoCp(CO)_3 + NaCl$ [4].

A subsection of this type of reaction is the "Grignard" reaction, involving the use of "metal carbonyl Grignard reagents", as in

$Mn(CO)_5MgBr + Ph_3SnBr \rightarrow (OC)_5MnSnPh_3 + MgBr_2$ [5].

2). Elimination reactions.

a) $CpFe(CO)_2{}_2 + 2HSiCl_3 \longrightarrow 2CpFe(CO)_2SiCl_3 + H_2$ [6].

b) $2HMn(CO)_5 + GeH_4 \longrightarrow H_2Ge(Mn(CO)_5)_2 + 2H_2$ [7].

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* Cp = π-cyclopentadienyl.

† Internal square brackets indicate bridging ligands.

c) $CpW(CO)_3H + Me_3SiNMe_2 \rightarrow CpW(CO)_3SiMe_3 + NMe_2H$ [3].

3). Ligand replacement reactions.

a) $(Me_3Sn)_2S + Cr(CO)_6 \rightarrow (Me_3Sn)_2SCr(CO)_5 + CO$ [8].

b) $Me_2Sn(PPh_2)_2 + Ni(CO)_4 \rightarrow Me_2Sn[PPh_2]_2Ni(CO)_2 + 2CO$ [9].

4). Oxidative addition reactions.

a) Trans-$(Ph_3P)_2(CO)IrCl + HgCl_2 \longrightarrow$

cis-$(Ph_3P)_2(CO)IrCl_2HgCl$ [10].

5). Oxidative elimination reactions.

a) $Fe(CO)_5 + HgCl_2 \longrightarrow Fe(CO)_4(HgCl)_2 +$ other products [11].

6). Insertion reactions.

a) $Zn + Mn_2(CO)_{10} \longrightarrow (OC)_5MnZnMn(CO)_5$ [12].

b) $Hg + CpFe(CO)[CO]_2Co(CO)_3 \longrightarrow CpFe(CO)_2HgCo(CO)_4$ [13].

7). Other reactions.

a) Cis-$(Et_3P)_2PtCl_2 + Me_3GeHgGeMe_3 \longrightarrow$

trans-$(Et_3P)_2PtClGeMe_3 + ClHgGeMe_3$ [14].

b) $(Ph_3P)_4Pt + 2Cl_3SiH \longrightarrow$

$(Ph_3P)_2Pt(SiCl_3)_2$ + other products[15].

(Reaction 7a could also be looked upon as a type of elimination reaction, as in 2, above).

Of the above reactions, 1 and 2 have been most widely used.

Turning now to the preparation of complexes containing only transition metals, reactions analogous to 1, 2, and 3 as listed above, have been found to be the most productive.

1). Nucleophilic displacement reactions.

a) $CpFe(CO)_2I + NaCo(CO)_4 \longrightarrow CpFe(CO)[CO]_2Co(CO)_3 + NaI$[16].

b) $Re(CO)_5Cl + NaMn(CO)_5 \longrightarrow (OC)_5MnRe(CO)_5 + NaCl$[17].

2). Elimination reactions.

a) $2(OC)_4FePPh_2H + [\pi\text{-}C_3H_5PdCl]_2 \longrightarrow$

$[(OC)_4Fe[PPh_2]PdCl]_2 + 2C_3H_6$[19].

b) $(OC)_4FePPh_2H + Cp_2Ni \longrightarrow$

$CpNi[CO][PPh_2]Fe(CO)_3 + C_5H_6$[18].

3). Ligand replacement reactions.

a) $CpTi(NMe_2)_3 + Mo(CO)_6 \longrightarrow CpTi\left[NMe_2\right]_3Mo(CO)_3 + 3CO$ [20].

b) $Cp_2Ti(SePh)_2 + Mo(CO)_6 \longrightarrow$

$$Cp_2Ti\left[SePh\right]_2Mo(CO)_4 + 2CO$$ [21].

c) $Cp_2W(SMe)_2 + Cr(CO)_6 \longrightarrow Cp_2W\left[SMe\right]_2Cr(CO)_4 + 2CO$ [22].

From the two lists of reactions shown above, it can be seen that the synthetic routes leading to the two classes of complexes are very similar. On the other hand, their chemical properties differ markedly.

Referring to the complexes containing both transition and main group metals, as X, and to those containing only transition metals, as Y, all of the complexes X listed above, with the exception of $(Me_3Sn)_2SCr(CO)_5$ and $Me_2Sn\left[PPh_2\right]_2Ni(CO)_2$, contain metal-metal bonds by which the main group metal and the transition metal are linked together. The complexes $(Me_3Sn)_2SCr(CO)_5$ and $Me_2Sn\left[PPh_2\right]_2Ni(CO)_2$ have, in -S- and $-PPh_2-$, respectively, ligands which form a bridge between the two metal atoms. None of the complexes X have both bridging ligands and metal-metal bonds.

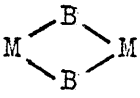
In complexes Y, it has been found that although some

contain only bridging ligands, e,g, $Cp_2W[SMe]_2Cr(CO)_4$, and some contain only metal-metal bonds, e.g. $MnRe(CO)_{10}$, in some cases, e.g. $CpFe(CO)[CO]_2Co(CO)_3$, it is necessary to postulate a metal-metal bond even though the complex has bridging ligands between the two metals. This postulate is made to explain the observed diamagnetism of such complexes.

For the present, it will be instructive if we consider some dinuclear metal carbonyl complexes in order to examine the need to postulate a metal-metal bond in certain complexes. $Mn_2(CO)_{10}$[23], $Re_2(CO)_{10}$[24], and $MnRe(CO)_{10}$[25] are isomorphous, and contain no bridging carbonyl groups, so that Mn-Mn, Re-Re, and Mn-Re bonds, respectively, must hold the two halves of the complexes together. The molecular structures of $Co_2(CO)_8$[26] and $Fe_2(CO)_9$[27] show that there are 2 and 3 bridging carbonyl groups, respectively, between the metals. Counting up the valence electrons in $Co_2(CO)_8$ and dividing by 2 to give the number of valence electrons surrounding each cobalt atom, gives 17 electrons, which is an odd number. Therefore, in $Co_2(CO)_8$ the odd electrons must be spin paired, giving a Co-Co bonding interaction to account for the observed diamagnetism. The same argument holds for $Fe_2(CO)_9$. The metal-metal interaction need not be strong to spin pair the electrons

and could, in fact, be transmitted through the bridging carbonyls using multi-centre molecular orbitals. However, the Co-Co distance of 2.52Å, and the Fe-Fe distance of 2.46Å, in $Co_2(CO)_8$ and $Fe_2(CO)_9$ respectively, indicate that in these complexes there is a strong, direct interaction between the two metals.

In complexes with bridging ligands other than carbon-monoxide, it is difficult to estimate the strength of the postulated metal-metal bond. In order to form a strong bond, the two metals must get as close together as possible, but in some cases limits are set on how close the two metal atoms can approach each other because of the bulk of the surrounding ligands.

Basing his arguments on X-ray crystallographic data Dahl[28] has suggested there is evidence in dinuclear complexes which require spin pairing, that the two metal atoms try to get as close together as possible. The outcome of this is that, in the central  ring

(M is a transition metal and B is a bridging ligand) the BMB angles tend to become obtuse and the MBM angles tend to become acute. The degree to which these angles become obtuse and acute, respectively, will not depend on the size of the bridging ligands, but the metal-metal distance

will depend on the size of these ligands. Thus, it is better to make estimates of the M-M bond strength by considering the bond angles in the 4 membered MBMB ring rather than considering the M-M distance.

In bridged complexes where it is not necessary to postulate a metal-metal bond, the MBM angles are obtuse, the BMB angles are acute, and the MBMB ring as a whole is planar[28].

The MBMB ring, in complexes with a metal-metal bond, has been found to be planar, as in $\left[Et_3PMo(CO)_3\left[PMe_2\right]\right]_2$[29], or puckered, as in $\left[Fe(CO)_3\left[SEt\right]\right]_2$[30]. Whether the ring is puckered or planar seems to depend on the co-ordination number of the metals in the ring[28].

In complexes with a central 4 membered ring of the type M(SR)M(SR), the -R groups can take up more than one orientation with respect to each other in relation to the MSMS ring, thereby raising the possibility of geometrical isomerism. This has been found to occur in $\left[(OC)_3Fe\left[SMe\right]\right]_2$[31] and related complexes[32].

Returning now to heterodinuclear complexes, which have, by definition, two different metal atoms, it should be possible to compare one side of the complex with the other in order to obtain information about any metal-metal

interaction which may occur.

Comparisons of this type can be carried out using infra-red, n.m.r., and ultra-violet/visible spectroscopic techniques as an alternative to complete elucidation of the molecular structure by diffraction techniques. The information which can be obtained from the various spectroscopic techniques will be considered in the following paragraphs.

The energies of the carbonyl stretching vibrations in binary metal carbonyls have been found to increase as the electronic charge on the central metal atom is decreased, thus, in $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ the carbonyl stretching frequencies are 1859, 2000, and 2096cm.$^{-1}$, respectively[33a]. The metal-carbon bond in metal carbonyls is considered to be made up of σ and π components: σ-donation of the lone pair on carbon into the vacant metal orbitals, and formation of a π-bond by back donation of electrons from the metal orbitals into the π^* antibonding orbitals on carbon monoxide. The formation of the π-bond is thought to be crucial since it removes electron density from the metal thereby stabilising its low oxidation state. σ and π effects are difficult to separate because of a synergic effect which strengthens the metal-carbon π-bond when the strength of the metal-carbon σ-bond is increased.

The overall result is that any factor which leads to increased electronic charge on the central metal atom will tend to decrease the carbonyl stretching frequencies, since the increased electron density on the metal will be transmitted, via a π-bond, into the π^*-antibonding orbitals on the carbonyl group[33].

In substituted metal carbonyls, the electronegativity of the substituent and its σ-donor and π-acceptor properties, as compared with those of carbon monoxide, will have a pronounced effect on the carbonyl stretching frequencies since each of these parameters will determine the charge on the metal atom. The factors which have an effect in the individual complexes, as far as their carbonyl stretching frequencies are concerned, will be discussed in Chapter 2.

The chemical shifts of the various protons in the ^{1}Hn.m.r. spectrum of a complex indicate the degree of shielding the individual protons feel. This gives some measure of the electron density at various points in the complex and thereby helps to elucidate the bonding system. Because of their great susceptibility to environment, the resonance positions of the protons are also very useful tools for elucidating the structures of isomeric complexes[31,32].

Far infra-red (400-40cm.$^{-1}$) and ultra-violet/visible spectroscopy have also been used in this research, but, as always, exact assignments of the peaks are difficult and not normally unambiguous. In the case of the far infra-red spectra this ambiguity stems from the fact that since most of the complexes studied are of such low symmetry, virtually every vibration is infra-red active. This leads to a very large number of peaks considering the numbers of atoms in the complexes. Comparisons of the spectra with those of mononuclear "parent" complexes are inconclusive since the "parents" do not necessarily have structures which are related to the dinuclear complexes (See Chapter 3).

The position is not quite so bad as far as ultra-violet/visible spectroscopy is concerned. The difficulty here is in deciding what observations made in the excited states of a molecule mean in its ground state.

Because of the range of physical properties, especially solubility, found in the various sets of complexes prepared in this research, different techniques have had to be used to elucidate the various structures and properties.

Chapter 2 deals with complexes which are, to some extent, soluble and therefore their solution spectra can be examined. A set of extremely insoluble Cu/Ti complexes are discussed in Chapter 3. The far infra-red spectra

of all the complexes prepared are discussed in Chapter 4.

Most of the complexes to be discussed were prepared by ligand replacement reactions involving the use of "transition metal containing ligands" from which the title "Organometallic Complexes as Ligands" is derived. These mononuclear complexes contain transition metals to which are bonded groups or atoms having at least one lone pair suitable for donation to another transition metal. The properties of these "ligands"are discussed in Chapter 1 to serve as a reference for subsequent chapters.

Those ligand replacement reactions which gave products derived by rearrangements or decompositions from the desired products are discussed in Chapter 5. The problems encountered when using nucleophilic displacement or elimination reactions as routes to heteronuclear complexes are also considered in Chapter 5.

CHAPTER 1

Transition Metal Containing Ligands

The main objectives of this research were to prepare and study multi-heteronuclear transition metal complexes. As will be seen in later chapters, most of these complexes were prepared by ligand replacement reactions, in which a "transition metal containing ligand" is used to replace ligands from another metal. Some of the properties of these "transition metal containing ligands" will now be discussed.

The mono-nuclear "ligands" are of two types:-

1). $(L\text{-}L)M(SR)_2$, (L-L = 1,2 bis-diphenylphosphino ethane, O-phenylene bis-diethylarsine; M = Pd, Pt; R = Me, Ph).

2). $Cp_2Ti(SR)_2$, (R = Me, Ph).

1). The complexes $(L\text{-}L)M(SR)_2$.

The complexes prepared together with data from their far infra-red, ^{1}Hn.m.r., and u.v./visible spectra are given in Table 1.1.

a) Preparation

(In this section L-L stands for any chelating diphosphine, diarsine, or disulphide, whereas in (b), L-L will be confined exclusively to 1,2 bis-diphenylphosphino ethane and O-phenylene bis-diethylarsine).

All the complexes listed in Table 1.1 were prepared by the general reaction,

$(L\text{-}L)MCl_2 + 2RSH + 2NEt_3 \longrightarrow (L\text{-}L)M(SR)_2 + 2NEt_3HCl$ (in toluene),

after preliminary reactions had shown that the other possible route to these complexes, i.e.

$(L\text{-}L)MCl_2 + 2NaSR \longrightarrow (L\text{-}L)M(SR)_2 + 2NaCl$ (in ethanol),

gave, as well as the desired products, considerable yields of water soluble products which could not be characterised.

The complexes $Me_2PCH_2CH_2PMe_2M(SR)_2$ (M = Pd, Pt; R = Me, Ph) were not obtained by either of the two methods described above; 100% yields of water soluble products were obtained in both cases.

The reasons for these 100% yields of water soluble (presumed ionic) products, and for the significant yields of similar products from the reactions of NaSR with $Ph_2PCH_2CH_2PPh_2MCl_2$ in ethanol, cannot be explained as the water soluble products could not be characterised. Products similar to these have been obtained, together with the desired products, in analogous reactions[34]. It is possible that the water soluble species may be intermediates which, when reacted with a suitable reagent, lead to the desired products (as is necessary in the preparation of some chelating diphosphine platinum dichloride complexes[35]) but, since the nature of the water soluble species is unknown, this is merely supposition.

In certain instances, when $(L\text{-}L)MCl_2$ was reacted with either i) NaSR or ii) RSH and NEt_3, the chelating ligand, L-L, was liberated and $\left[M(SR)_2\right]_n$[36] was formed. The reactions in which this occurred were those involving $Ph_2PCH_2PPh_2PdCl_2$, 1,5-hexadienePtCl$_2$, $PhSCH_2CH_2SPhPdCl_2$

(when reacted with NaSMe, or MeSH and NEt_3), and $MeSCH_2CH_2SMePdCl_2$ (when reacted with NaSPh, or PhSH and NEt_3).

The preferred formation of $[M(SR)_2]_n$ and L-L rather than $(L\text{-}L)M(SR)_2$ (for a given R) will occur because the lone pairs on sulphur (in $(L\text{-}L)M(SR)_2$) are strong enough nucleophiles to displace the chelating ligand from the metal. Since $Ph_2PCH_2PPh_2$, $PhSCH_2CH_2SPh$, and $MeSCH_2CH_2SMe$ are displaced from palladium, whereas $Ph_2PCH_2CH_2PPh_2$ and $C_6H_4(AsEt_2)_2$ (o-phenylene bis-diethylarsine) are not, the former group of chelating ligands must be less strongly bonded to palladium than are those in the latter group.

In an attempt to rationalise these observations the metal-chlorine stretching frequencies of the complexes $(L\text{-}L)MCl_2$ were recorded, and are listed in Table 1.2. There does not, however, seem to be any correlation between either or both of the metal-chlorine stretching frequencies and the course of the reactions.

In the absence of any π-bonding effects in the M-Cl and M-L bonds, it might have been anticipated that the metal-chlorine stretching frequencies would be directly related to the strength of the σ-bonds from L-L to the metal: the stronger the M-L σ-bond the lower the metal-chlorine stretching frequency. But, because of the possibilities of π-bonding and synergic effects, increased

π-backbonding from M to L with better σ-donors would tend to raise the metal-chlorine stretching frequencies. Thus, if both the σ-donor and π-acceptor properties of the donating atoms in L-L determine the M-L bond strength in $(L\text{-}L)MCl_2$, it is hardly surprising that the metal-chlorine stretching frequencies do not give an indication of the strengths of the M-L bonds. So, for a given complex $(L\text{-}L)MCl_2$ it is not possible to tell a priori whether the desired complex, $(L\text{-}L)M(SR)_2$, will be formed or whether the chelating ligand, L-L, will be liberated, in the reaction of $(L\text{-}L)MCl_2$ with SR^-.

b) Properties.

The infra-red, ^{1}Hn.m.r., and u.v./visible spectroscopic data to be discussed are listed in Table 1.1.

i) Infra-red Data

The metal-sulphur(methyl) stretching frequencies were assigned unambiguously by comparison of the corresponding diarsine and diphosphine complexes.

Both the symmetric and asymmetric metal-sulphur(methyl) stretching vibrations occur at very similar frequencies when M = Pd and when M = Pt for a given chelating ligand. This result is the same as that observed for the metal-

Table 1.1

Complex	ν_{M-S}[a] ($cm.^{-1}$)	^{1}Hn.m.r. τ_{S-CH_3}[b]	U.V./Visible Spectra $\nu_{max.}$ ($cm.^{-1}$)(log ε)[c]
$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$	320, 307	7.98	22000(2.32);24300(2.43); 29700(4.07);38000(4.68);
$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$	326, 309	7.88	26100(2.15);32700(3.56); 38700(4.45).
$Ph_2PCH_2CH_2PPh_2Pd(SPh)_2$			21200(3.03);29800(4.09); 37800(4.48).
$Ph_2PCH_2CH_2PPh_2Pt(SPh)_2$			25000(2.53);32600(3.80); 38900(4.58).
$C_6H_4(AsEt_2)_2Pd(SMe)_2$	318, 308	7.60	22700(2.48);28900(3.56); 35700(3.40).
$C_6H_4(AsEt_2)_2Pt(SMe)_2$	327, 318	7.40	>25600[d];30500(3.08); 37000(3.73).
$C_6H_4(AsEt_2)_2Pd(SPh)_2$			21600(3.14);29200(3.71); 35900(3.66).

a) Recorded as "Rigidex" discs.

b) In $CDCl_3$, using internal T.M.S. = 10.0 τ as standard.

c) In $CHCl_3$.

d) Exact position and extinction coefficient were not obtained because of the proximity of the intense peak at 30500cm.$^{-1}$.

The ligands $Ph_2PCH_2CH_2PPh_2$ and $C_6H_4(AsEt_2)_2$ show only weak bands in the range covered.

Table 1.2

Complex	ν M-Cl ($cm.^{-1}$)[a]	
$Ph_2PCH_2CH_2PPh_2PdCl_2$	310	286[b]
$Ph_2PCH_2CH_2PPh_2PtCl_2$	314	293
$C_6H_4(AsEt_2)_2PdCl_2$	319	300
$C_6H_4(AsEt_2)_2PtCl_2$	320	302
$Me_2PCH_2CH_2PMe_2PdCl_2$	300	268
$Me_2PCH_2CH_2PMe_2PtCl_2$	301	277
1,5-hexadiene$PtCl_2$	340	316
$MeSCH_2CH_2SMePdCl_2$	315	296[b]
$PhSCH_2CH_2SPhPdCl_2$	338	318

a) Recorded as "Rigidex" discs.

b) Recorded as Nujol mulls (Ref. 37).

chlorine stretching frequencies in $(L\text{-}L)MCl_2$. (See Table 1.2)

ii) ^{1}Hn.m.r. Data

The resonances of the $-S-C\underline{H}_3$ protons in $(L\text{-}L)M(SMe)_2$ are at higher field when M= Pd than when M= Pt, suggesting that in the bonds joining the sulphur atoms to the metal, the electronic charge is more concentrated round the sulphur atoms when M= Pd than when M= Pt. This means, effectively, that in $(L\text{-}L)M(SMe)_2$, Pt is more electronegative than Pd, for a given L-L.

iii) U.V./Visible Data

If the above argument, concerning the relative electronegativities of Pd and Pt, is correct, metal→ligand charge transfer in $(L\text{-}L)M(SR)_2$ should be of lower energy when M= Pd than when M= Pt, for a given L-L and R. Of the 3 bands (4 in the case of $PPh_2PCH_2CH_2PPh_2Pd(SMe)_2$) the 2 at higher energy (29,000-33,000cm.$^{-1}$ and 35,000-39,000cm.$^{-1}$) can be assigned to charge transfer bands because of their high extinction coefficients. Since both of these bands occur at lower energies when M= Pd than when M= Pt, they are thought to arise from metal to ligand charge transfer. These assignments are very tentative, and therefore no attempt has been made to

investigate the nature of the molecular orbitals involved. The other (low energy, low extinction coefficient) band (2 in the case of $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$) in the range 21,000-26,000cm.$^{-1}$ is assigned to a d→d transition. These bands also follow the above pattern in frequency differences on going from Pd to Pt, but this is probably fortuitous as the higher energy transition in the platinum complexes is probably associated with the greater ligand field splitting in the third row element. Bands in the electronic spectra of some dinuclear π-allyl palladium complexes have recently been assigned[40], but the positions and assignments differ somewhat from those described above.

iv) Bonding in $(L\text{-}L)M(SR)_2$

The complexes are thought to have an approximately square planar arrangement of ligands around the central metal atom. With this arrangement of ligands, 8 of the 9 bonding molecular orbitals, constructed from the (n-1)d, ns, and np atomic orbitals of Pd or Pt, and the ligand orbitals, will be filled, but the 9th orbital will be vacant since the metal atom in $(L\text{-}L)M(SR)_2$ is surrounded by only 16 valence electrons. In the co-ordinate axes of Figure 1.1 this vacant orbital will approximate to a pure np_z orbital (because of the higher energy associated with

the np orbitals as compared with the (n-1)d orbitals) lying perpendicular to the plane of the ligands. This vacant orbital may not be absolutely pure np_z as there may be a small contribution from the ligand orbitals.

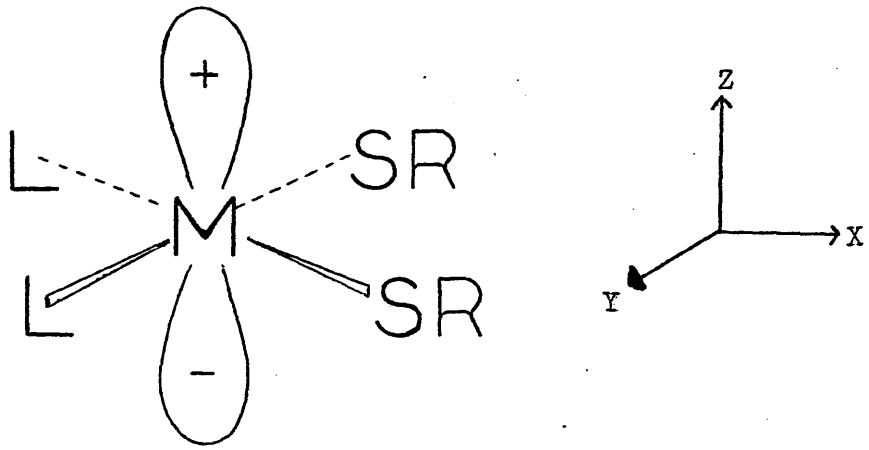


Figure 1.1 The vacant orbital in $(L\text{-}L)M(SR)_2$.

2). The complexes $Cp_2Ti(SR)_2$:

a) Preparation

The complexes $Cp_2Ti(SR)_2$ (R= Me,Ph) were prepared by the general reaction:-

$Cp_2TiCl_2 + 2RSH + 2NEt_3 \longrightarrow Cp_2Ti(SR)_2 + 2NEt_3HCl$. (in toluene).

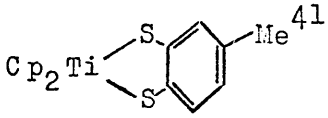
The preparation of the complexes $Cp_2Ti(SR)_2$ by the reaction of Cp_2TiCl_2 with NaSR in toluene gave, as well

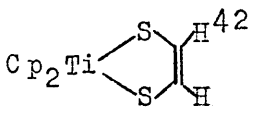
as the desired products, products containing a TiOTi sequence[39]. The reactions of $NaC{\equiv}CPh$ with Cp_2TiCl_2 also gave products contaminated with oxygen. Similarly, when $ZrCl_4$ was reacted with NaC_5H_5[38], products containing ZrOZr were obtained. These observations can only be rationalised by assuming that a reduction step is taking place giving Ti^{III} which is re-oxidised, by atmospheric oxygen, on work up, to give Ti^{IV}-O-Ti^{IV}. Giddings[39] found that Cp_2TiCl_2 was easily reduced by zinc dust, but the reduction would not take place when metallic sodium was used instead. Thus, although reduction must be taking place, it is not possible to say whether the reducing agent is finely divided sodium (possibly catalysed by the sodium salts, NaSR) or the sodium salts themselves.

In some reactions of Cp_2TiCl_2 with $NaC{\equiv}CPh$, complexes were obtained which gave analytical figures close to those required for $Cp_2Ti(Cl)C{\equiv}CPh$. This suggests that the first chlorine atom is more easily replaced than the second. It has been found[41] that the reactions of Cp_2TiCl_2 with α,ωdithiols, in the presence of base, yielded oligomers of the general formula $Cl\text{-}TiCp_2\text{-}\left[S\text{-}(CH_2)_n\text{-}S\text{-}TiCp_2\right]_x\text{-}S\text{-}TiCp_2Cl$ instead of the desired products, $Cp_2Ti(S\text{-}(CH_2)_n\text{-}S)$. This again indicates that the first chlorine atom is more easily replaced than the second, by the incoming nucleophile. It is therefore inferred that the tarry products from the

reactions of Cp_2TiCl_2 with $HSCH_2CH_2SH$, in the presence of NEt_3, are also oligomers.

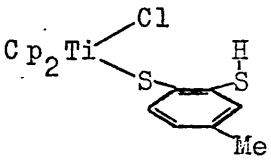
It should be pointed out, that complexes of the desired type are known, although they are systems such as

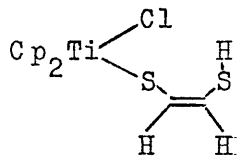


[41] and


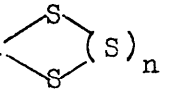
[42]

where there is much more rigid steric control over the orientations the free thiol can adopt relative to the other chlorine atom in the probable intermediates



and


.

However, the related complexes $Cp_2M(SCH_2CH_2S)$ (M = Mo, W)[43] and  ($n = 1, 2, 3$)[44,45] have been reported, and there may be factors other than steric control involved in these cases.

The failure to prepare $CpTi(SMe)_3$ at room temperature agrees with the report[46] that $CpTi(SPh)_3$ is unstable above -25°C. Razuvaev and Latyaeva[47] have pointed out that the complexes $CpTiX_3$ are, in general, unstable as compared with Cp_2TiX_2. (X = an alkyl or aryl radical, a halogen, or an alkoxide group).

b) Properties

The ^{1}Hn.m.r. and u.v./visible spectroscopic data for the complexes $Cp_2Ti(SR)_2$, together with similar data for Cp_2TiCl_2 and $Cp_2Ti(OPh)_2$, are listed in Table 1.3. (The far infra-red data will be discussed in Chapter 4).

i) ^{1}Hn.m.r. Data

The positions of the cyclopentadienyl proton resonances in $Cp_2Ti(SR)_2$ (R = Me, Ph) are in agreement with published data for these and related complexes[41,48-50]. The main feature of the spectra is a shift to higher field of the single cyclopentadienyl proton resonance signal on going from Cp_2TiCl_2 to $Cp_2Ti(SR)_2$. Cyclopentadienyl protons have been found to resonate at higher field as the electronegativity of the other substituents on titanium is reduced[51-53]. Therefore, chlorine being more electronegative than sulphur (the electronegativity of the latter may well vary slightly with small changes in inductive and mesomeric effects of the groups R in $Cp_2Ti(SR)_2$) the shift to higher field is as expected.

A single cyclopentadienyl proton resonance is observed for both $Cp_2Ti(SMe)_2$ and $Cp_2Ti(SPh)_2$ even at -35°C in chlorobenzene (See Table 2.1, Chapter 2) indicating that in both complexes the two rings are magnetically equivalent and are not restricted in their rotation by the -SR groups.

Table 1.3

Complex	^{1}Hn.m.r. Spectra.[a]				U.V./Visible[b] Spectra.
	$\tau C_5\underline{H}_5$		$\tau S\text{-}C\underline{H}_3$		$\nu max.(cm.^{-1})$
	$CDCl_3$	C_6H_5Cl	$CDCl_3$	C_6H_5Cl	$(\log \varepsilon)$.
Cp_2TiCl_2	3.40	c	-	-	19300(3.35); 26100(2.31).
$Cp_2Ti(OPh)_2$	3.70	c	-	-	d
$Cp_2Ti(SMe)_2$	3.88	4.24	7.38	7.43	18800(3.62); 27600(3.06).
$Cp_2Ti(SPh)_2$	3.97	4.24	-	-	18600(3.60); 26000(3.23).

a) Relative to internal T.M.S. at 10.0τ.

b) In $CHCl_3$.

c) $C_5\underline{H}_5$ resonance too close to $C_6\underline{H}_5Cl$ resonance to be distinguished.

d) No absorption between 14000 and 25000cm.$^{-1}$. Strong absorption above 26400cm.$^{-1}$.

Two cyclopentadienyl proton resonances have been observed[45] at room temperature in the spectrum of Cp_2TiS_5 in which, as shown in Figure 1.2, the two cyclopentadienyl rings are in different environments since inversion of the S_5Ti ring is slow (relative to the ^{1}Hn.m.r. time scale) or non-existant. The two signals coalesce at higher temperatures indicating that more rapid inversion is taking place. Similar results have been observed[54] for CH_2S_5.

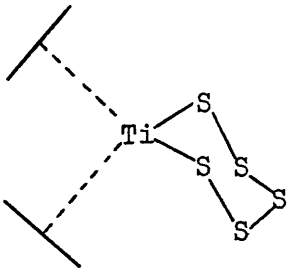


Figure 1.2 Orientations of the Cp rings in Cp_2TiS_5.

ii) U.V./Visible Data

Attempts have been made[38,55] to assign bands in the electronic spectra of the complexes Cp_2MX_2 (M = Ti, Zr; X = Cl, Br), but the assignments are inconclusive since the relative energies of the molecular orbitals involved are virtually unknown. Only qualitative assignments for the complexes $Cp_2Ti(SR)_2$ have therefore been attempted.

The high intensities of the two bands observed below

28,000cm.$^{-1}$ suggests that they can be assigned to ligand $\longrightarrow$ metal charge transfer, rather than to internal excitation of the cyclopentadienyl or phenyl (when R = Ph) rings. Cp_2TiCl_2 and $Cp_2Ti(SR)_2$ both show bands in the region 18-19,000cm.$^{-1}$ whereas $Cp_2Ti(OPh)_2$ does not. On the basis that the differences in these spectra must arise from differences in ligands other than the cyclopentadienyl rings, the peaks at 18,800cm.$^{-1}$ in $Cp_2Ti(SMe)_2$ and at 18,600cm.$^{-1}$ in $Cp_2Ti(SPh)_2$ are assigned to sulphur $\longrightarrow$ titanium charge transfer. The other peaks, at 27,600cm.$^{-1}$ in $Cp_2Ti(SMe)_2$ and at 26,000cm.$^{-1}$ in $Cp_2Ti(SPh)_2$, are assigned to charge transfer from the cyclopentadienyl rings to titanium.

iii) Bonding in $Cp_2Ti(SR)_2$

The scheme proposed by Ballhausen and Dahl[56] for bonding in Cp_2MoH_2 and related complexes, consists of forming 9 hybrid orbitals from the (n-1)d, ns, and np metal orbitals. Of these hybrid orbitals, 3 point towards each of the cyclopentadienyl rings and 3 lie in the plane bisecting the angle formed by the intersection of the planes of the two rings.

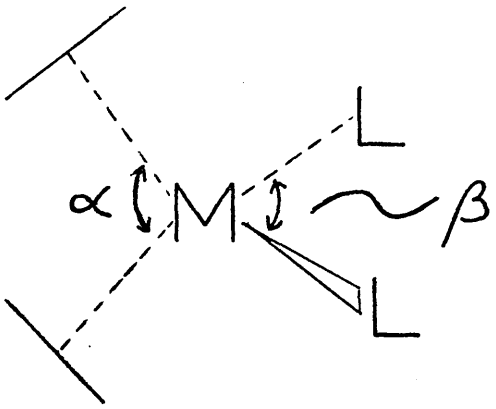
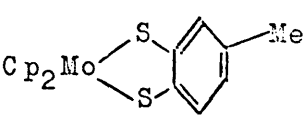


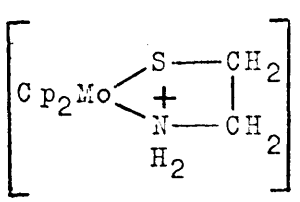
Figure 1.3 Hypothetical $Cp_2M^{IV}L_2$ complex.

The angle α (Figure 1.3), according to Ballhausen and Dahl's scheme, should lie between 135° and 180°, and β should be 150° (approx.). In the complex Cp_2MoH_2 α is found[57] to be 146°, which is within the predicted limits.

In the molybdenum complexes, the above theory predicts that the lone pair of molybdenum electrons should bisect angle β and lie in the ML_2 plane, giving high electron density between the two L groups.

By considering structural data for similar complexes e.g.

a) Cp_2Mo  ($\alpha = 132.5°$; $\beta = 82.4°$)[58]

b)  ($\alpha = 130.9°$; $\beta = 78.4°$)[59]

it has been argued[58,59] that β is too small to permit the presence of a localised lone pair between the two sulphur atoms in (a) or between the sulphur and nitrogen atoms in (b). (See Previous page).

An alternative bonding scheme, similar to that proposed[60] for $Cp(MeC_5H_4)ReMe_2$, allowing more delocalisation of the lone pair and less severe restrictions on the values of α and β, has therefore been suggested[58] for the above complexes.

In the complexes $Cp_2Ti(SR)_2$, the orbital analogous to that which contains the lone pair in Cp_2MoL_2, is empty since the titanium complexes are only 16 electron systems. The molecular structure of the complex Cp_2TiS_5 shows[61] that $\alpha = 133.6^\circ$ and $\beta = 94.6^\circ$. Since, in this complex, α and β are outside the limits predicted by Ballhausen and Dahl's theory, the vacant orbital on titanium may well be delocalised in a manner similar to the probable delocalisation of the lone pair on molybdenum in Cp_2MoL_2.

CHAPTER 2

Heterodinuclear Complexes.

In this chapter the preparation and properties of the complexes bis-π-cyclopentadienyl titanium di-μ-organothio tetracarbonyls of Group VI, $Cp_2Ti\left[SR\right]_2M'(CO)_4$, I, (R = Me, Ph; M' = Cr, Mo, W) and chelating diphosphine or diarsine palladium^{II} or platinum^{II} di-μ-organothio tetracarbonyls of Group VI, $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, II, (L-L = 1,2 bis-diphenylphosphino ethane, o-phenylene bis-diethylarsine; M = Pd, Pt; R = Me, Ph; M' = Cr, Mo, W) will be discussed. The infra-red, ^{1}Hn.m.r., and u.v./visible spectra of complexes I and II will be compared and contrasted with similar data for the "transition metal containing ligands", (See Chapter 1), and those of the mononuclear complexes $RSCH_2CH_2SRM'(CO)_4$, III, (R = Me, Ph; M' = Cr, Mo, W).

The structures and bonding systems in I and II will be considered in the light of the known structure of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$[62].

As the preparations of I and II are similar, they can be treated together, but the properties of I and II are very different and will, therefore, be discussed separately.

1) Preparation of the Complexes $Cp_2Ti[SR]_2M'(CO)_4$ (I), and $(L\text{-}L)M[SR]_2M'(CO)_4$ (II).

As can be seen from the Experimental (Sections 7 and 8) complexes I and II were prepared by ligand replacement reactions in which the "transition metal containing ligands", $Cp_2Ti(SR)_2$ and $(L\text{-}L)M(SR)_2$, were reacted at room temperature with norbornadiene-$M'(CO)_4$. Co-ordinated norbornadiene has the property, necessary in ligand replacement reactions, of being easily replaced. An exactly analogous reaction has recently been used to prepare $MeSeCH_2CH_2SeMeCr(CO)_4$ from $MeSeCH_2CH_2SeMe$ and norbornadiene-$Cr(CO)_4$[63].

Replacement of norbornadiene has the advantage that very mild reaction conditions can be used and high yields of the products, without much decomposition, were obtained for most of the reactions attempted. The ease of replacement of norbornadiene from norbornadiene-$M'(CO)_4$ was found to decrease in the order Mo > W > Cr, and hence

reaction times required were least for M' = Mo and greatest for M' = Cr. The reaction between $Cp_2Ti(SPh)_2$ and norbornadiene-$Cr(CO)_4$ gave none of the desired product, and on heating, only decomposition products were obtained. It was found, in general, that reactions in which R = Me were faster than those in which R = Ph, for a given Group VI metal.

Reactions of the rather insoluble $Ph_2PCH_2CH_2PPh_2M(SPh)_2$ (M = Pd,Pt) with norbornadiene-$M'(CO)_4$ (M' = Cr,W) yielded no dinuclear products. On the other hand, although the reactions of $C_6H_4(AsEt_2)_2Pd(SR)_2$ with norbornadiene-$M'(CO)_4$ (M' = Cr,W) went rapidly, the products decomposed, as they were slightly soluble in toluene, which was used as solvent for all preparations of complexes I and II.

Another way round the problem of preparing fairly labile complexes of this type, by ligand replacement reactions, is to react the ligand with the Group VI hexacarbonyl in ultra-violet light. This proceedure has been used[21] to prepare one of the complexes, $Cp_2Ti\left[SPh\right]_2Mo(CO)_4$, which will be discussed in this chapter.

It had been hoped to use $Cp_2Ti(C{\equiv}CPh)_2$ as a ligand which would co-ordinate onto the Group VI metal through the acetylenic groups as has been observed elsewhere with pure acetylenes[98] and vinyl silanes[99], but, as was observed in

Chapter I, $Cp_2Ti(C{\equiv}CPh)_2$ was not obtained in a pure state.

2) Properties of bis-π-cyclopentadienyl titanium di-μ-organothio tetracarbonyls of Group VI, $Cp_2Ti\left[SR\right]_2M'(CO)_4$, I, (R = Me,Ph; M' = Cr,Mo,W)

The infra-red carbonyl stretching frequencies and stretching parameters, ^{1}Hn.m.r. data, and transitions observed in the electronic spectra (14,000-30,000cm.$^{-1}$) of the complexes $Cp_2Ti\left[SR\right]_2M'(CO)_4$, I, are listed in Table 2.1, together with similar data for the mononuclear complexes $RSCH_2CH_2SRM'(CO)_4$, III, and $Cp_2Ti(SR)_2$. The infra-red carbonyl stretching frequencies and stretching parameters of the complexes cis-$(AsEt_3)_2Mo(CO)_4$[64], $C_6H_4(AsMe_2)_2Mo(CO)_4$[65], and $Me_2Si\left[AsEt_2\right]_2Mo(CO)_4$[9] are also included for comparison.

The stretching parameters (average force constants) listed in Table 2.1, and elsewhere throughout this chapter are given by the expression[66]

$$\bar{k} = \sum_i g_i\lambda_i \,/\mu_i\sum g_i \qquad \text{m.D./A.}$$

where the summation runs over all CO stretching modes i of degenaracy g_i and $\lambda_i/\mu_i = 4.0383\times10^{-6}\nu_i^{\,2}$ (ν_i being the

TABLE 2.1

Table 2.1 Complexes I, $Cp_2Ti[SR]_2M'(CO)_4$, and related complexes.

	Infra-red Spectra.			Proton n.m.r. Spectra.[h]						Electronic Spectra.[j]		
				-35°C		20°C		50°C				
	$\nu(C\equiv O)$ ($cm.^{-1}$) $CHCl_3$ Soln.	k^f	Δk^g	$C_5\underline{H}_5$	$S\text{-}C\underline{H}_3$	$C_5\underline{H}_5$	$S\text{-}C\underline{H}_3$	$C_5\underline{H}_5$	$S\text{-}C\underline{H}_3$	νmax. ($Cm.^{-1}$) (logε)	High Energy[k] Shoulder ($cm.^{-1}$) Visual Estimate.	Resolved Lowest[l] Energy Peak ($cm.^{-1}$) (log ε)
R = Me, M' = Cr	2000, 1908, 1892.			4.80(s) 4.86(s) 4.97(s)	7.55	4.79(s) 4.86(br) 4.98(s)	7.55	4.83(br)	7.55	23300 (3.44) 15700		15600 (3.65)
R = Me, M' = Mo	2071, 2016, 1918, 1903.	15.80	0.73	4.75(s) 4.84(s) 4.95(s)	7.50	4.74(s) 4.94(s)	7.50	4.80(br)	7.48	24800 (3.54) 16900	18900	16500 (3.73)
R = Me, M' = W	2070, 2010, 1910, 1890.	15.69	0.72	4.77(s) 4.86(s) 5.00(s)	7.42	4.78(s) 4.88(s) 5.00(s)	7.43	4.82(br)	7.38	24800 (3.70) 16900	19100	16400 (3.61)
R = Ph, M' = Mo	2018, 1930, 1912, 1899.	15.17	0.16			4.82(br)				25000 (3.63) 17100	19100	16000 (3.69)
R = Ph, M' = W	2017, 1919, 1900, 1888.	15.16	0.17			4.85(br)				26200 (3.65) 17000	19000	16000 (3.65)
$MeSCH_2CH_2SMeCr(CO)_4$[a]	2020, 1914, 1898, 1869.	14.98					7.65(s)[i]			26300 (2.60)		
$MeSCH_2CH_2SMeMo(CO)_4$[a]	2030, 1919, 1905, 1868.	15.07					7.56(s)[i]			27600 (3.20)		
$MeSCH_2CH_2SMeW(CO)_4$[a]	2023, 1910, 1897, 1867.	14.97								27000 (3.30)		
$PhSCH_2CH_2SPhMo(CO)_4$	2027, 1905(br) 1870.	15.01								27700 (3.15)		
$PhSCH_2CH_2SPhW(CO)_4$	2023, 1914, 1899, 1868.	14.99								27700 (3.16)		
$Cp_2Ti(SMe)_2$				4.16(s)	7.40	4.24(s)	7.43			27600 (3.06) 18800 (3.62)		
$Cp_2Ti(SPh)_2$				4.25(s)		4.24(s)				26000 (3.23) 18600 (3.60)		
cis-$(AsEt_3)_2Mo(CO)_4$[b]	2015, 1915, 1904, 1886.	15.05										
$C_6H_4(AsMe_2)_2Mo(CO)_4$[c]	2026, 1938, 1923, 1914.	15.37										
$Me_2Si[AsMe_2]_2Mo(CO)_4$[d]	2015, 1896, 1882, 1856.	14.78										

a. Infra-red spectrum from ref.70.

b. Spectrum from ref.64. (n-hexadecane).

c. Spectrum from ref.9. (Cyclohexane).

d. Spectrum from ref.65. (Nujol Mull).

e. Highest energy peak 5-10 times weaker than others. Highest energy peak not observed in $Cp_2Ti\left[SMe\right]_2Cr(CO)_4$. (See Figure 2.3)

f. See text.

g. $\Delta k = k_{Cp_2Ti\left[SR\right]_2M'(CO)_4} - k_{RSCH_2CH_2SRM'(CO)_4}$. (br = broad peak).

h. In Chlorobenzene, except where otherwise stated, (i), τ values relative to internal T.M.S. at 10.0τ.

i. In $CDCl_3$ solution. Proton resonance of $\underline{H}_3CSCH_2CH_2S\underline{CH}_3$ (uncomplexed) is at 7.85τ in $CDCl_3$. (ref.70). (s = singlet, br = broad peak).

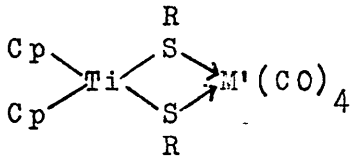
j. In $CHCl_3$ solution.

k. See text.

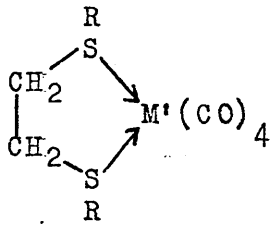
l. See text and Figure 2.1.

wavenumber ($cm.^{-1}$) of the $\underline{i}^{th}$ mode). The determination of $\bar{k}$ involves neglect of anharmonicity, and of coupling of CO modes with other modes. but is independent of the form assumed by the CO-CO interaction force field. Here, in the notation of Cotton and Kraihanzel[67], $k=(k_1+k_2)/2$.

The data given in Table 2.1, together with the analytical figures of complexes I, suggest a structure such as Ia which can be compared with the probable structure of complexes III, III.



Ia



III

a) Infra-red Data.

It has been shown[33] that the electron demand of the subtituent in a substituted metal carbonyl, has a direct effect on the infra-red carbonyl stretching frequencies. A substituent which wants a lot of electron density around it will tend to pull electrons out of the t_{2g} orbitals on the metal. Since these electrons would otherwise be used for $d\pi$-$p\pi$ metal to carbon backbonding, the metal-carbon bonds are weakened and the carbon-oxygen bonds are

strengthened, thereby raising the carbonyl stretching frequencies. A substituent which does not require much electron density around it will not exert such a pull on the t_{2g} electrons, thus allowing more backbonding to take place, which strengthens the metal-carbon bond and weakens the carbon-oxygen bond causing the carbonyl stretching frequencies to be lowered.

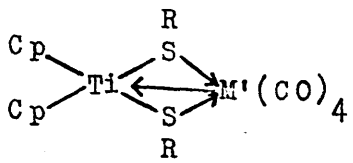
The desire of substituents to be surrounded by high or low electron density will approximate to the electronegativities of the substituents, but the actual electronegativities of the free ligands will be modified by the proximity of the metal to which the ligand is co-ordinated as, in most cases, the ligand has to donate electrons to, and accept electrons from the metal. The ability of a substituent to donate and accept electrons will be dependent on the orbitals which are available, and some ligands will be better equipped in this respect, than others. Thus, although electronegativities will be used in the following argument, the conclusions reached will only approximate to the correct ones.

From Table 2.1, it can be seen that the carbonyl stretching frequencies and stretching parameters of $Me_2Si\left[AsMe_2\right]_2Mo(CO)_4$ are lower than those of <u>cis</u>-$(AsEt_3)_2Mo(CO)_4$ and $C_6H_4(AsMe_2)_2Mo(CO)_4$. Introduction of

silicon (electronegativity 1.74) in place of carbon (electronegativity 2.50) (electronegativities are those given by the Allred-Rochow formula[68,69]) has therefore had the predicted effect of lowering the carbonyl stretching frequencies and stretching parameters.

Although no similar data are available for chelating disulphides, on general grounds it might have been thought that complexes I would have lower carbonyl stretching frequencies and stretching parameters than complexes III since the electronegativity of titanium is only 1.32. However, inspection of Table 2.1 shows exactly the opposite effect: the carbonyl stretching frequencies and parameters are higher in I than in III.

Electronegativity differences cannot be the only factor involved since this result requires that the electron density on M' in I is lower than on M' in III. This can only be achieved by donation of electrons from M' to titanium as shown in Ib.



Ib

b) ^{1}Hn.m.r. Data.

The ^{1}Hn.m.r. spectra of complexes I show 3 main effects:-

i) The cyclopentadienyl proton resonances are at higher field in I than in $Cp_2Ti(SR)_2$.

ii) The S-methyl proton resonances are at higher field in I (R = Me) than in $Cp_2Ti(SMe)_2$. (This effect is small though measurable for M' = Cr,Mo, but barely significant for M' = W).

iii) In I (R = Me) 3 separate peaks are observed for the cyclopentadienyl protons. Although the signals were too close together to allow integration, the cyclopentadienyl resonances appear to show two peaks of equal intensity with another (smaller) peak in between these.

If the chemical shift is taken as a measure of electron density around the cyclopentadienyl and S-methyl protons in $Cp_2Ti(SMe)_2$, one might have expected that both these resonances would be shifted to lower field on formation of complexes I since one of the lone pairs, initially localised on sulphur, is now used to form a S$\rightarrow$M bond.

A downfield shift has been observed[70] in the ligand methyl resonances on formation of III (R = Me) as compared

with the free ligand. The smallness of this shift probably arises from the effect noted in the previous paragraph and backbonding from M' to sulphur almost cancelling each other out. Such backbonding would be smaller, and the corresponding downfield shift larger in I than in III, since the Ti-S bonds will be polarised more in the sense $\overset{\delta+}{Ti}-\overset{\delta-}{S}$ than the C-S bonds.

The effects (i) and (ii) noted above show that simple sulphur σ-donation to M' cannot be the only factor involved, and M'$\longrightarrow$Ti donation, as in Ib, must again be considered.

For R = Me, the differences in stretching parameters between I and III are greater than for R = Ph. This would appear to indicate greater M'$\longrightarrow$Ti donation in I when R = Me than when R = Ph. However, the upfield shift of the cyclopentadienyl proton resonance on going from $Cp_2Ti(SR)_2$ to complexes I is the same for R = Me and for R = Ph. This would seem to indicate equal degrees of M'$\longrightarrow$Ti donation in these two cases. These differing results could be rationalised in terms of differing S(R)$\longrightarrow$M' σ-donation, though comparison of III (R = Me) with III (R = Ph) gives no support for this suggestion. Alternatively, there may be different solvent effects on the ^{1}Hn.m.r. spectra of $Cp_2Ti(SR)_2$ on complex formation.

The splitting of the cyclopentadienyl proton resonance

signal in complexes I may be explained in terms of geometrical isomerism. (See (d), Structure and Bonding, below).

c) Electronic Data.

There is a marked colour change on conversion of $Cp_2Ti(SR)_2$ (purple) to complexes I (blue, or for M' = Cr, green), and this colour change cannot simply be assigned to an $L_2M'(CO)_4$ chromophore since complexes III are yellow. In order to quantify this observation, the u.v./visible absorption spectra (chloroform solution) of complexes I, III, and $Cp_2Ti(SR)_2$ were recorded. Diffuse reflectance spectra were also recorded and are very similar to the solution spectra. The two strong bands observed in $Cp_2Ti(SR)_2$ (in the range 14,000-30,000cm.$^{-1}$) have already been assigned to ligand $\longrightarrow$ titanium charge transfer. (See Chapter 1).

The most marked difference between the spectra of $Cp_2Ti(SR)_2$ and those of complexes I is a shift to lower energy of both bands accompanied by an apparent broadening, incipient splitting, and an increase in intensity of the lower energy band. The low energy feature of complexes I seems to contain at least 2 separate absorptions.

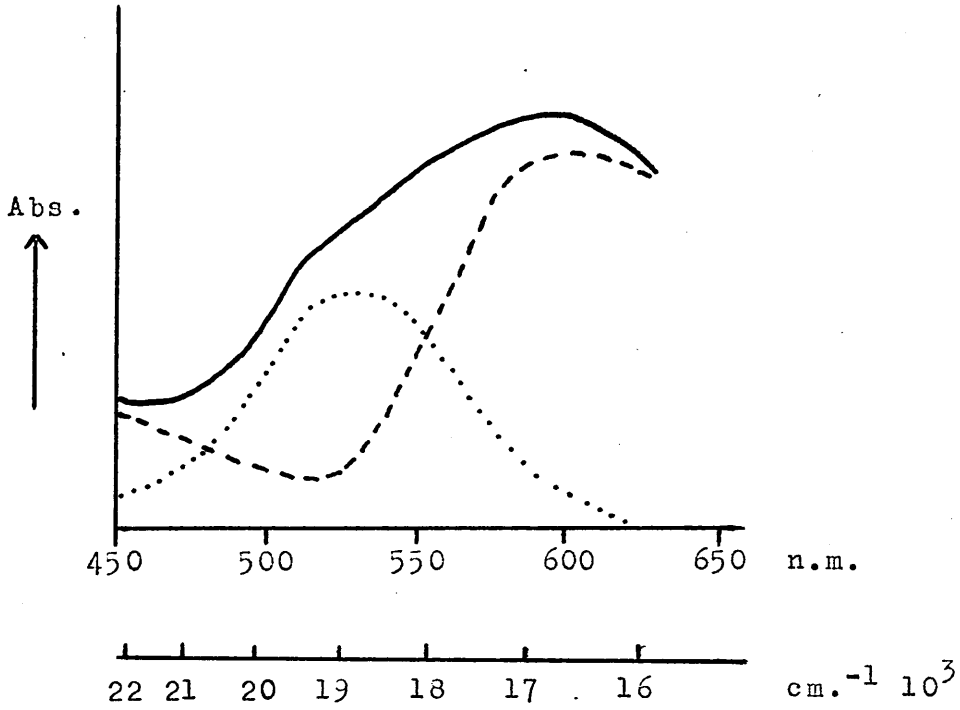
Graphical analysis of this feature (by "mirror imaging"

the long wavelength tail of the more intense low energy component) gave a high energy component in a very similar position (approx. 18,000cm.$^{-1}$) to that already assigned to an S⟶Ti charge transfer band in $Cp_2Ti(SR)_2$. (Chapter 1) It is inferred that this high energy component is the original S⟶Ti charge transfer band of $Cp_2Ti(SR)_2$, virtually unchanged after complexation.

The low energy component was analysed more quantitatively by subtracting from the observed spectra of complexes I, the absorption, corrected for concentration, assignable to the $Cp_2Ti(SR)_2$ chromophore alone. This proceedure seems to have been remarkably successful in view of the crudity of the assumptions involved; a typical analysis is shown in Figure 2.1. The positions and extinction coefficients of the bands obtained in this manner are listed in Table 2.1 under the heading "Resolved lowest energy peak".

This new band in complexes I is not present in either of the chromophores $Cp_2Ti(SR)_2$ or $L_2M'(CO)_4$ (complexes III show only one band which can be assigned to charge transfer from sulphur to M'). The new band is not thought to be a weak band of either isolated chromophore which gains in intensity on formation of complexes I for 2 reasons. Firstly, the bands are extremely intense and secondly,

Figure 2.1



⟵⟶ = experimental spectrum of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$.

⟵····⟶ = spectrum of $Cp_2Ti(SMe)_2$ corrected for concentration.

⟵----⟶ = curve obtained by subtracting spectrum of $Cp_2Ti(SMe)_2$ from spectrum of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$.

there is virtually no loss of symmetry around Ti and M' on formation of complexes I as compared with $Cp_2Ti(SR)_2$ and $RSCH_2CH_2SRM'(CO)_4$. (See (d), Structure and Bonding, below).

The new band is therefore assigned to a transition involving both of the metal atoms. It could be regarded as a charge transfer band (or possibly, in the formalism of Ib, a $\sigma \longrightarrow \sigma^*$ or $\sigma \longrightarrow n$ transition). The high intensity of this band indicates that the transition moment can be assigned considerable 1-centre character and hence overlap or mixing of the orbitals on the two metals must be appreciable.

Although electronic spectra can never give direct information about bonding in the ground state, this result is consistent with (and, if no other information were available, would suggest) considerable metal-metal bonding.

Another point arising from the electronic spectra of complexes I is that the higher energy band, at 27,600cm.$^{-1}$ in $Cp_2Ti(SMe)_2$ and at 26,000cm.$^{-1}$ in $Cp_2Ti(SPh)_2$, has moved to lower energy onformation of complexes I. If, as suggested in Chapter 1, this band can be assigned to charge transfer from the cyclopentadienyl rings to titanium, it is possible to argue that since titanium is now receiving electrons from M', charge transfer from the rings to

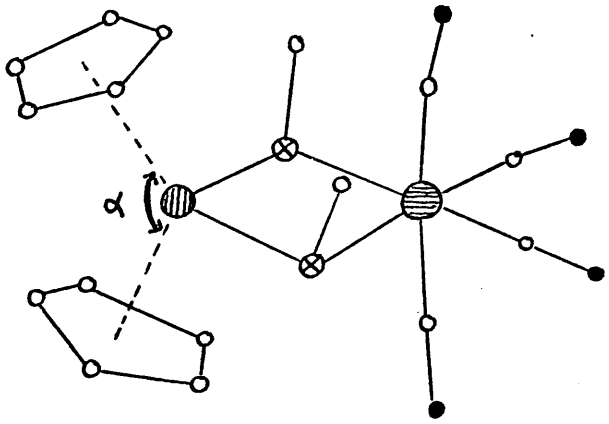
titanium should move to higher energy. On the other hand, the presence of more electronic charge on the rings, as shown by the upfield shift of the cyclopentadienyl proton resonances may make charge transfer from the rings to titanium move to lower energy. Comparison of the frequencies at which the corresponding charge transfer occurs in Cp_2TiCl_2 snd $Cp_2Ti(SR)_2$ shows them to be very similar, (See Table 1.3) although the cyclopentadienyl proton resonances are at lower field in the former. This suggests that there is no simple relationship between the chemical shifts of the cyclopentadienyl protons and the energy of charge tranfer from the rings to titanium. Similarly, in complexes I, there does not seem to be any correlation between the charge transfer from the rings to titanium and from M' to titanium.

d) Structure and Bonding.

The molecular structures of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$ [62] (A) and Cp_2TiS_5 [61] (B) are shown in Figure 2.2 and Table 2.2 lists some of the corresponding bond lengths and angles.

The main point that emerges from a comparison of A and B, is that the two bridging sulphur atoms in A are being forced apart. This widening of the S-Ti-S angle leads to a contraction of α in A as compared with the

Figure 2.2



= Mo

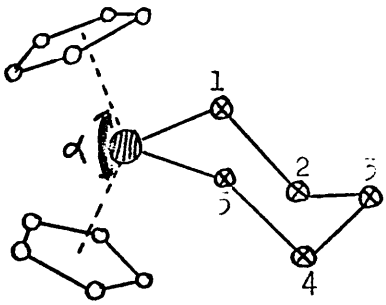
= Ti

= S

= C

= O

Structure of $Cp_2Ti[SMe]_2Mo(CO)_4$ (A).



Structure of $Cp_2Ti(SMe)_2$ (B).

Table 2.2 Comparison of some bond lengths and bond angles in $Cp_2Ti[SMe]_2Mo(CO)_4$ (A) and Cp_2TiS_5 (B). (See also Figure 2.2)

	A	B
$\hat{STiS}$	99.9°	94.6° ($S_1\hat{TiS}_5$)
α	129°	133.6°
$\hat{TiSMo}$	83°	
$\hat{SMoS}$	94.6°	
$\hat{TiS_1S_2}$		107°
S---S (non-bonded)	3.78Å	3.58Å (S_1---S_5)
Ti-Mo	3.32Å	

Table 2.3 Bond angles in some dinuclear complexes.

Complex	$\hat{MBM}$	$\hat{BMB}$
$\left[(OC)_3Fe\left[PMe_2\right]\right]_2$ M = Fe, B = P	102.4°	77.4°
$\left[(OC)_4Mn\left[Br\right]\right]_2$ M = Mn, B = Br	96°	82°
$\left[Et_3P(OC)_3Mo\left[PMe_2\right]\right]_2$ M = Mo, B = P	78.2°	101.9°
$\left[SnMe_3(OC)_3Ru\left[SnMe_2\right]\right]_2$ M = Ru, B = Sn	71.5°	108.5°

corresponding angle in B. These comparisons added to the facts that the S-Mo-S angle has been opened up from a probable 90° in III to 94.6° in A and that the Ti-S-Mo angle in A is only 83° as compared with 107° for the $Ti-S_1-S_2$ angle in B, suggest that the metal atoms are trying to get as close together as possible.

All the bridged dinuclear transition metal complexes requiring metal-metal bonds, for which structures are known, show effects similar to those noted above, i.e. the M-B-M angles become acute and the B-M-B angles become obtuse in the central MBMB ring. This point can be illustrated by the bond angles found in the complexes listed in Table 2.3. The complexes $\left[(OC)_3FeI\left[PMe_2\right]\right]_2$[71] and $\left[(OC)_4Mn\left[Br\right]\right]_2$[72] have no metal-metal bonds whereas $\left[(Et_3P)(OC)_3Mo\left[PMe_2\right]\right]_2$[29] and $\left[SnMe_3(OC)_3Ru\left[SnMe_2\right]\right]_2$[74] have metal metal bonds. Each of the complexes has a planar MBMB ring.

The crystal structure of $SnMe_3(OC)_3Ru\left[SnMe_2\right]_2Ru(CO)_3SnMe_3$ is particularly interesting since the C-Sn-C angle in the $SnMe_2$ bridge is 109° whereas the Ru-Sn-Ru angle is 71.5°. This shows that the Sn-C bond, and hence the Sn-Ru bond are still formed from sp^3 hybridised tin, but the attractive force between the two Ru atoms is strong enough to contract the Ru-Sn-Ru angle by some 37.5°.

The Mo-Ti distance of 3.32Å in $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$ seems very long compared with metal-metal bond lengths in related complexes (normally in the range 2.5-3.0Å, although longer bonds have been observed in complexes of 2nd and 3rd row elements) but, as pointed out by Dahl[28] and others[29], there are restraints on the closeness of approach of the two metal atoms. The factor which normally determines the metal-metal bond length is the size of the bridging atom: the larger the atom the longer the metal-metal bond. Thus, in a hypothetical case, a chlorine-bridged complex will have a shorter metal-metal bond than the corresponding iodine-bridged complex, simply because of the greater bulk on iodine as compared with chlorine.

Since sulphur is a relatively small atom, and Fe-Fe distances of 2.72Å and 2.54Å have been observed in $\left[(ON)_2Fe\left[SEt\right]\right]_2$[75] and $\left[(OC)_3Fe\left[SEt\right]\right]_2$[30], respectively, (the latter cannot constitute an exact analogy since the FeSFeS ring is puckered) a shorter Mo-Ti distance might have been expected if the size of the bridging atom was the only factor involved in determining the Mo-Ti bond length. In $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$, it is not so much the size of the bridging atom, but the steric interactions between the two cyclopentadienyl rings that are thought to determine the Mo-Ti bond length. If the Ti and Mo atoms

were moved closer together the S-Ti-S angle would have to become more obtuse, leading to further closing of α resulting in very close approach of the cyclopentadienyl rings.

There may also be a steric repulsive force acting between the two halves of the complex across the TiSMoS ring on the side of the S-methyl groups since the carbonyl group attached to Mo on this side of the ring is pushed away from the ring. Such a force would also oppose closer approach of the metals.

The similarity between the solution spectra and the diffuse reflectance spectra of A and of related complexes examined, and the general similarities in the physical properties of these complexes, indicate that there is no major change in solution and that all the complexes I may be presumed to have a basically similar structure.

The cyclopentadienyl proton resonances (as shown in Figure 2.4) observed in the ^{1}Hn.m.r. spectra of complexes I (R = Me) may readily be understood if geometrical isomerism takes place. Cisoid (1c) and transoid (1d) isomers (Figure 2.5) are present, the former, which is found in the solid, being predominant.

Interchange of the two isomers is slow or non-existant

Figure 2.3 Infra-red carbonyl stretching frequencies in $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$.

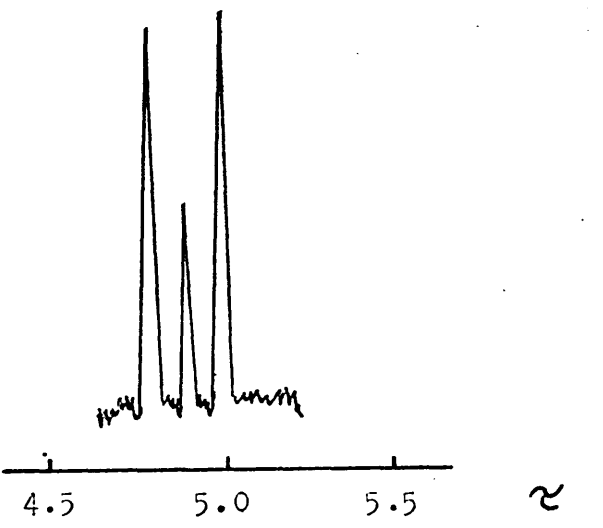
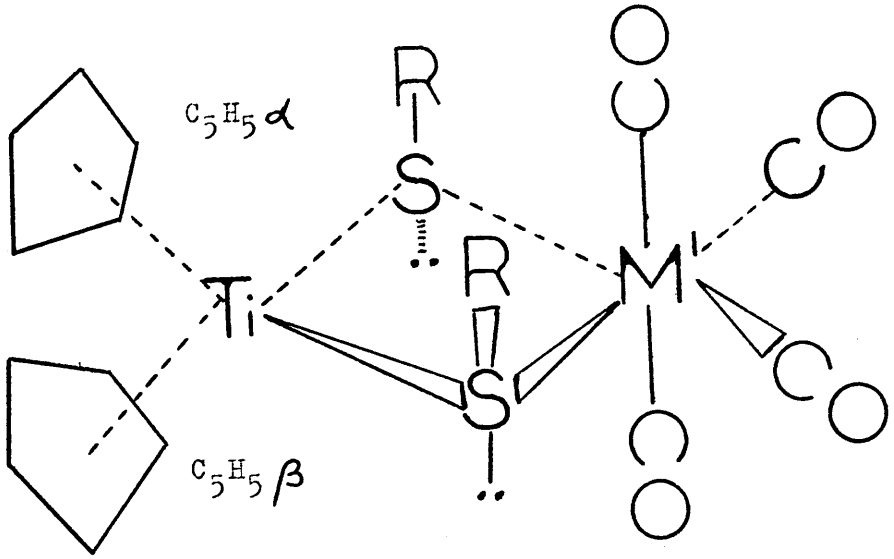
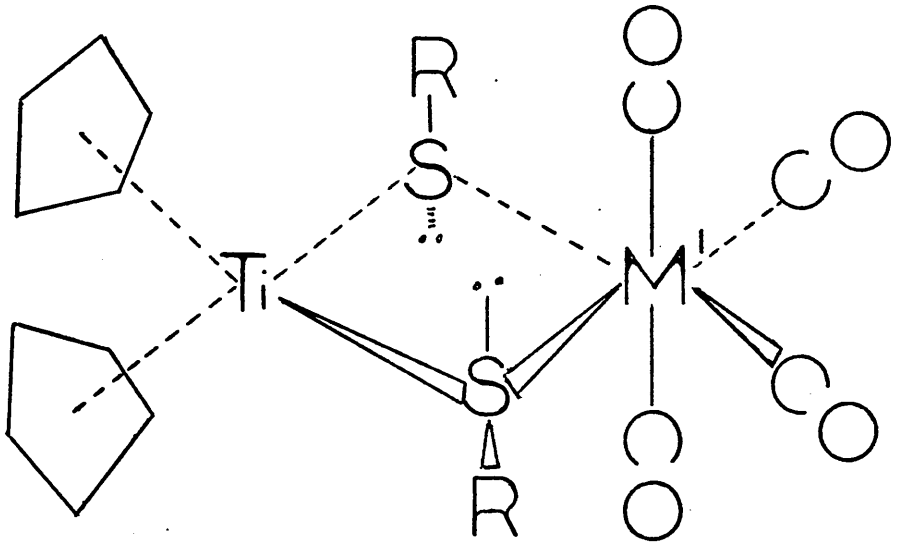


Figure 2.4 ^{1}Hn.m.r. spectrum of the cyclopentadienyl protons in $Cp_2Ti\left[SMe\right]_2W(CO)_4$



Ic



Id

Figure 2.5 Geometrical isomerism in $Cp_2Ti[SR]_2M'(CO)_4$.

below 20°C, but rapid (on the ^{1}Hn.m.r. time scale) at 50°C. H_α is in a detectably different environment from H_β since the effects of a substituent at sulphur differ from those of a lone pair. This accounts for the two strong peaks of Figure 2.4, and can be compared with the resonances observed in Cp_2TiS_5 and CH_2S_5 (See Chapter 1). The weaker peak in between these is due to the ring protons (both sets of which are equivalent) of 1d. Since the S-methyl protons experience virtually the same environment in 1c and 1d, the methyl proton resonances cannot be separated.

Spectra of the complexes I (R = Ph) could not be obtained at -35°C because of their insolubility in chlorobenzene at this temperature. At 20°C a single rather broad peak (half peak height width around 3Hz.) was observed for the cyclopentadienyl ring protons. Since it seems unlikely that interconversion of isomers would be faster for the phenyl than for the methyl derivatives, it is inferred that the phenyl derivatives are present almost exclusively in the transoid form (1d) at room temperature. This difference in behaviour between methyl and phenyl complexes may be assigned to steric repulsion in the hypothetical species 1c, R = Ph.

The spectroscopic data for complexes I indicate an

appreciable amount of metal-metal interaction and, taking into account the structure of $Cp_2Ti[SMe]_2Mo(CO)_4$, a direct metal-metal bond is suggested. It could still be argued, however, that the metal-metal interaction might be relayed through the vacant sulphur 3d-orbitals. Direct interaction is favoured because a strong tendecy to relay electron density through the sulphur 3d-orbitals would probably tend to shield the S-methyl protons to a greater extent than is observed. (An accurate estimate of the amount of shielding felt by the S-methyl protons cannot, in fact, be made as the chemical shifts of the S-methyl protons in the hypothetical species (1a), where there is no M'$\longrightarrow$Ti donation, are unknown). The small upfield shift that is observed is thought to arise from the increase in electron density in the TiSM'S ring as a whole, brought about by the formation of the M'$\longrightarrow$Ti bond.

As pointed out in Chapter 1, the titanium atom in $Cp_2Ti(SR)_2$ has a vacant orbital. This orbital, still present in complexes I, can be equated (Table 2.4) with a d-orbital, or a 3d, 4s, $4p_z$ hybrid (in the co-ordinate system of Figure 2.6) directed towards M'. This orbital can accept electron density from the $d(z^2-x^2)$ orbital on M' to form the M'$\longrightarrow$Ti bond which is responsible for the unusual properties of complexes I. (The unusual label,

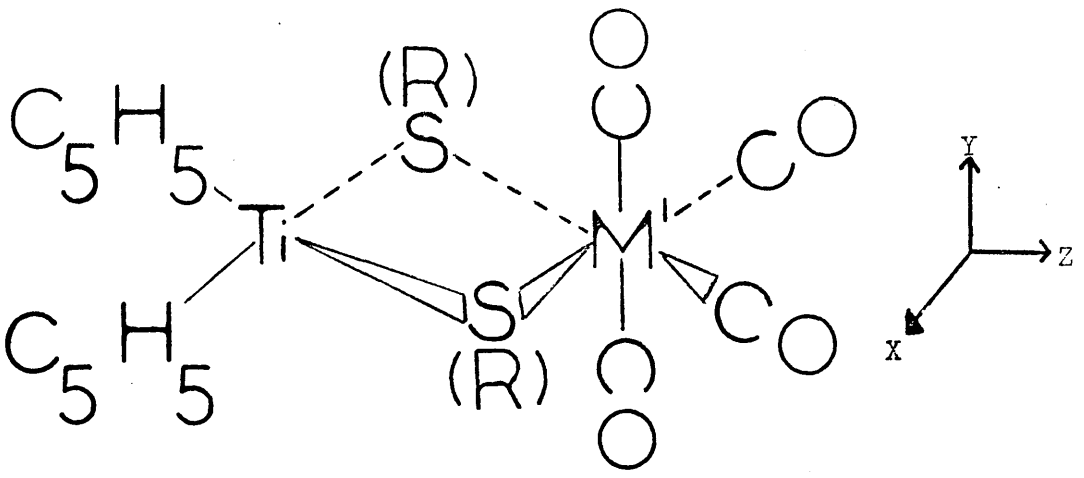


Figure 2.6 Co-ordinate axes for discussion of bonding in $Cp_2Ti[SR]_2M'(CO)_4$.

Table 2.4

Orbitals		Representations Spanned
$C_5H_5(a_1)$		$a_1 + b_2$
$C_5H_5(e(z))$		$a_1 + b_2$
$C_5H_5(e(x))$		$a_2 + b_1$
S-Ti		$a_1 + b_1$
Ligand Orbitals		$3a_1 + a_2 + 2b_1 + 2b_2$
Ti	3d	$2a_1 + a_2 + b_1 + b_2$
	4s	a_1
	4p	$a_1 + b_1 + b_2$
Metal Orbitals		$4a_1 + a_2 + 2b_1 + 2b_2$
Vacant Metal Orbital		a_1

$d(z^2-x^2)$, for a $d(t_{2g})$ orbital is an artefact of the co-ordinate system).

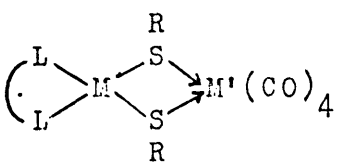
Dative metal-metal bonds, formed by a transition metal complex acting as a Lewis base, are fairly common in complexes containing a main or post transition group element and a transition metal, but are rare for complexes containing only transition metals. Cp_2MoH_2 and Cp_2WH_2 have been used extensively as Lewis bases, forming complexes such as $Cp_2WH_2BF_3$[76], $Cp_2WH_2AlMe_3$[77], and $Cp_2MoH_2Mo(CO)_5$[78]. $CpCo(CO)_2$ has similarly been used, forming complexes, mainly with mercuric halides, of the type $CpCo(CO)_2HgCl_2$[79]. There is no reason to suppose that the "dative" bond formed in the above complexes is any different from the normal, covalent type of metal-metal bond, e.g. the Co-Hg bond length in $CpCo(CO)_2HgCl_2$ is 2.58Å[80] as compared with 2.50Å in $(Co(CO)_4)_2Hg$[81]. A related type of bond is that formed between two atoms of the same metal, but in different oxidation states, as found[82] in $(OC)_3FeC_6H_8O_2Fe(CO)_3$, where there is donation from Fe^0 to Fe^{II}. The Fe-Fe bond length of 2.49Å is similar to normal Fe-Fe bond lengths in organometallic complexes. Metal-metal "dative" bonds have now come to be accepted, so much so that Lewis basicity has been the subject of a recent review[83].

It should, in conclusion, be mentioned, as has been pointed out elsewhere[21], that because electrons are being donated to M' by sulphur, and to Ti by M', the assignment of oxidation states to Ti and M' in complexes I is uncertain and probably arbitrary, although the two components used in the preparations, $Cp_2Ti(SR)_2$ and norbornadiene-$M'(CO)_4$, contain Ti^{IV} and M'^{0} respectively.

3) Properties of Chelating Diphosphine or Diarsine Palladium^{II} or Platinum^{II} di-μ-organothio tetracarbonyls of Group VI, $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, II, (L-L = 1,2 bis diphenylphosphino ethane, O-phenylene bis-diethylarsine; M = Pd, Pt; R = Me, Ph; M' = Cr, Mo, W).

The complexes $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, II, prepared, with their infra-red carbonyl stretching parameters and frequencies, and diffuse reflectance u.v./visible spectra are given in Table 2.5 together with similar data for related complexes.

These data, together with the analytical figures of complexes II are consistent with structure IIa.



IIa

TABLE 2.5

Table 2.5 Complexes II, $(L\text{-}L)M[SR]_2M'(CO)_4$ and related complexes.

P—P = $Ph_2PCH_2CH_2PPh_2$ As—As = $C_6H_4(AsEt_2)_2$	Infra-red Spectra.			Electronic Spectra.	
	$\nu(C\equiv O)(cm.^{-1})$ [b] $CHCl_3$ Soln.	$\bar{k}$	$\Delta\bar{k}$ [d]	νmax. Diffuse Reflectance Spectra($cm.^{-1}$)	νmax. Spectra from $CHCl_3$ Soln. ($cm.^{-1}$) (log ε)
P—PPd $[SMe]_2Cr(CO)_4$	1978, 1856, 1849, 1806. [c]			22500	
P—PPd $[SMe]_2Mo(CO)_4$	2003, 1893, 1863, 1823.	14.53	0.54	22700	
P—PPd $[SMe]_2W(CO)_4$	1994, 1890(br) 1833.	14.40	0.57	22200	
P—PPt $[SMe]_2Cr(CO)_4$	1994, 1884, 1861, 1817.	14.42	0.57	22700	
P—PPt $[SMe]_2Mo(CO)_4$	2005, 1893, 1860, 1817.	14.49	0.58	23500	
P—PPt $[SMe]_2W(CO)_4$	1998, 1881, 1853, 1811.	14.38	0.59	24100	
As—AsPd $[SMe]_2Mo(CO)_4$	2004, 1886, 1851, 1810.	14.41	0.66	23000	
P—PPd $[SPh]_2Mo(CO)_4$	2003, 1890, 1861, 1820.	14.50	0.51		
P—PPt $[SPh]_2Mo(CO)_4$	2006, 1891, 1864, 1827.	14.55	0.46		
As—AsPd $[SPh]_2Mo(CO)_4$	2008, 1896, 1864, 1821.	14.55	0.46	21000	
P—PPd$(SMe)_2$				22400 24400	22000 (2.32) 24300 (2.43)
P—PPd$(SPh)_2$					21200 (3.04)
P—PPt$(SMe)_2$				25900	26000 (2.15)
P—PPt$(SPh)_2$					25000 (2.53)
As—AsPd$(SMe)_2$				22800	22700 (3.15)
As—AsPd$(SPh)_2$				22500	21600 (3.15)
$MeSCH_2CH_2SMeCr(CO)_4$ [a]	2020, 1914, 1898, 1869.	14.98			26300 (2.60)
$MeSCH_2CH_2SMeMo(CO)_4$ [a]	2030, 1919, 1905, 1868.	15.07			27600 (3.2)
$MeSCH_2CH_2SMeW(CO)_4$ [a]	2023, 1910, 1897, 1867.	14.97			27000 (3.30)
$PhSCH_2CH_2SPhW(CO)_4$	2027, 1905(br) 1870.	15.01			27700 (3.15)

a. Infra-red spectrum from ref.70.

b. All peaks are strong. The peaks belonging to complexes II were determined by running successive spectra, and removing those peaks which gained in intensity. A typical spectrum is shown in Figure 2.8.

c. Nujol mull, complex too unstable in $CHCl_3$

d. $\Delta\bar{k} = \bar{k}_{RSCH_2CH_2SRM'(CO)_4} - \bar{k}_{(L\text{-}L)M[SR]_2M'(CO)_4}$

(br broad peak)

a) Infra-red Data.

The infra-red carbonyl stretching frequencies and stretching parameters of complexes II are lower than those of complexes III ($RSCH_2CH_2SRM'(CO)_4$). Thus, the introduction of an element, Pt or Pd, less electronegative than carbon, has the predicted effect of lowering the carbonyl stretching frequencies and stretching parameters. (See 2a, Infra-red Data, above).

b) Electronic Data.

The diffuse reflectance electronic spectra of complexes II are similar to the solution spectra (Chapter 1) and the diffuse reflectance spectra of $(L\text{-}L)M(SR)_2$ in the range 14,000-30,000cm.$^{-1}$. The lowest energy peaks (22,000-26,000cm.$^{-1}$) in $(L\text{-}L)M(SR)_2$ have been assigned (Chapter 1) to a d⟶d transition in M. The transitions observed in complexes II are in approximately the same positions as those in $(L\text{-}L)M(SR)_2$ when M = Pd, but are at slightly lower energy when M = Pt. The bands in complexes II are therefore assigned to a d⟶d transition in M. They are not assigned to a transition involving M' since the bands observed in the solution spectra of complexes III occur at somewhat higher energy ($\approx$27,000cm.$^{-1}$).

A "tailing off" effect on the low energy side of the observed bands in complexes II may arise from crystal effects since the spectra are those of solids, or the "tail" may be made up of weak, spin forbidden d⟶d transitions in M or M'. As this "tailing off" effect is more marked when M'= W than when M'= Cr,Mo, it is suggested that the transitions involve electrons on M', and that the transitions are more marked when M'= W because of increased spin-orbit coupling in the 3rd row element[84]. Therefore, if the "tail" arises from genuine transitions and not from crystal scattering effects, the transitions are tentatively assigned to spin forbidden d⟶d transitions in M'.

From the infra-red and electronic data, the properties of complexes II are consistent with structure IIa, where there is simple σ-donation from sulphur to M'.

The ^{1}Hn.m.r. spectra of complexes II were not obtained because of their rapid decomposition in solution. Had these spectra been obtained, it would have been possible to compare them with those of complexes I. Such a comparison might well have given a better idea of the chemical shifts of the S-methyl protons in the hypothetical species Ia, and hence a more accurate estimate of the shielding of the S-methyl protons in Ib might have been possible. (See 2d, Structure and Bonding, above).

c) Structure and Bonding.

The MBMB ring, in all bridged dinuclear complexes where no metal-metal bond is postulated, has been found to be planar. As the infra-red and electronic data give no evidence for a metal-metal bond in complexes II, the MSM'S rings are expected to be planar. Also, the SMS and SM'S angles are expected to be acute since M and M' will tend to repel each other as they each have electron pairs which point towards each other in the plane of the ring.

In some cases, the repulsive forces between the two metal atoms are strong enough to confer a polymeric, rather than dimeric, structure on the complex, as has been found, for example, in $((ON)_2CoI)_n$[28]. A polymeric structure, as in Figure 2.7, is thought unlikely to be the structure of complexes II since such a structure would have higher entropy than the dimeric structure, IIa, because the "ligands", $(L\text{-}L)M(SR)_2$, are no longer chelating. Also, a polymeric structure would probably make complexes II more insoluble than is observed. (Complexes II are fairly soluble in polar solvents, but decomposition is rapid thereafter). A polymeric structure such as shown in Figure 2.7, cannot be ruled out solely on infra-red evidence as this polymeric structure is derived from cis-substitution of the metal hexacarbonyl, as is IIa, and would probably give rise to a

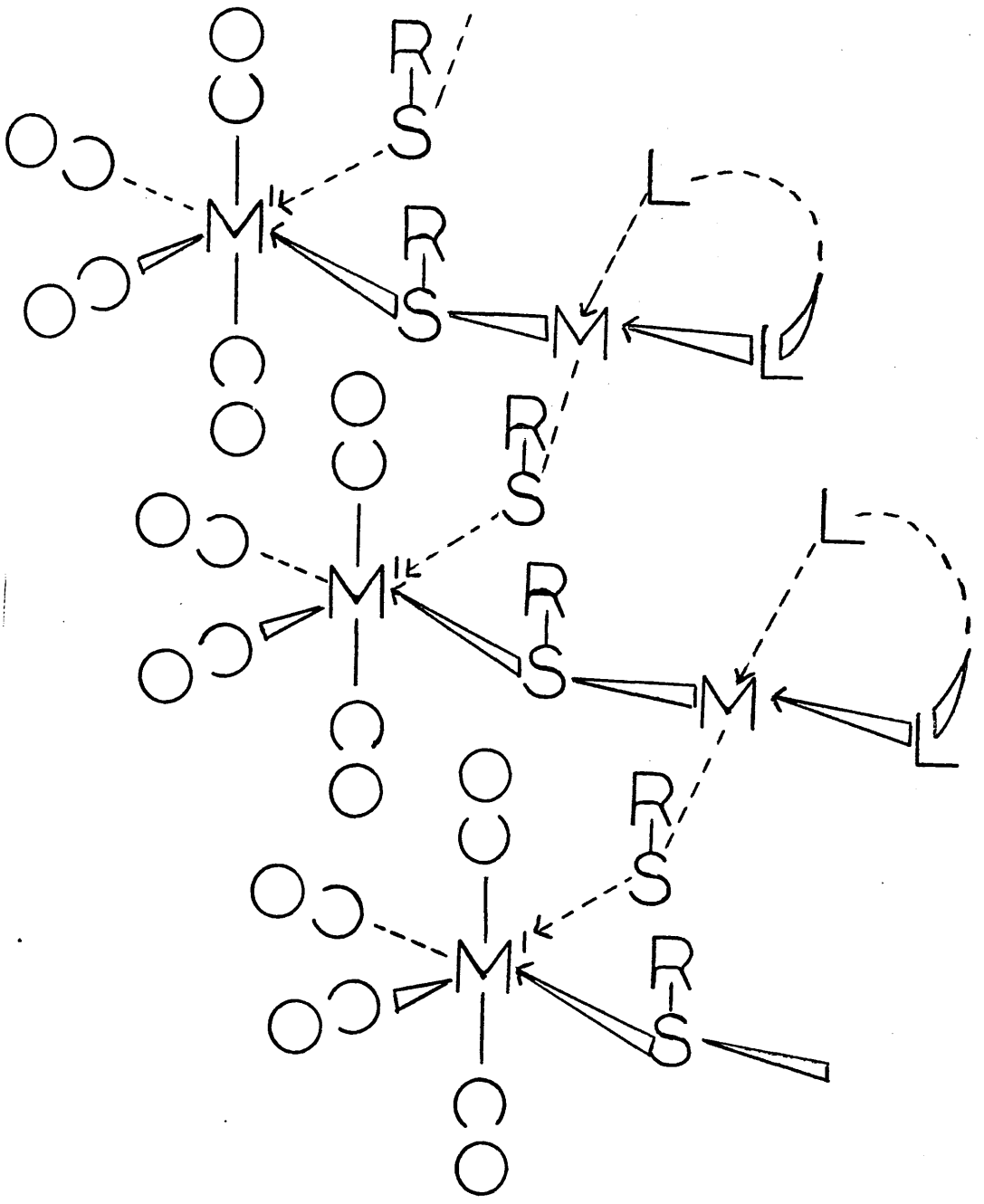
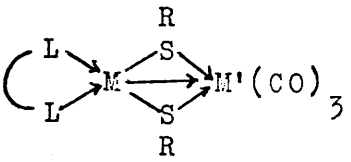


Figure 2.7 Possible polymeric structure for complexes II.

carbonyl stretching frequency pattern similar to that observed. (A typical spectrum is shown in Figure 2.8).

There is a possibility that the complexes $(L\text{-}L)M(SR)_2$ could behave as 6 electron donors, using, in addition to the lone pairs on sulphur, one of the lone pairs on M, giving a complex such as II'.



II'

II' cannot be ruled out on the basis of analytical figures for complexes II since the carbon analyses for II and II' differ by only 0.5%. Also, determination of %CO in dinuclear complexes of this type has been found[85] to give irreproducible results. II' can, however, be ruled out because of the observed number and pattern of carbonyl stretching frequencies in complexes II.

The orbitals on M and M' in complexes II which are directed towards each other are filled, so that, as well as tending to push the two metals apart, there may be a tendency for the electron pairs to be concentrated on their respective metals. This means that M', in complexes II, may well feel a higher electron density than in complexes III, not only because of electronegativity differences,

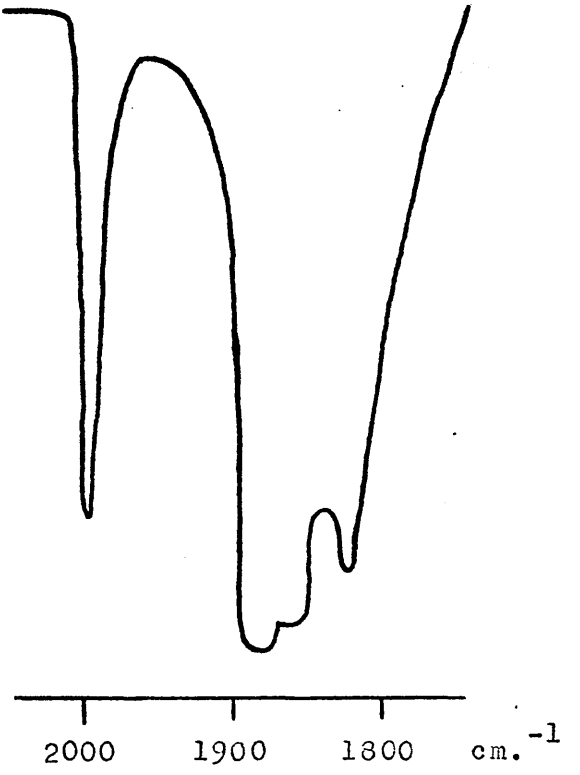


Figure 2.8 Infra-red carbonyl stretching frequencies in $Ph_2PCH_2CH_2PPh_2Pt\left[SMe\right]_2W(CO)_4$.

but also because of this trans-annular repulsion effect. Therefore, in complexes II both decreased electronegativity and repulsive effects may contribute to the overall lowering of the carbonyl stretching frequencies and parameters as compared with those of complexes III.

The carbonyl stretching frequencies and stretching parameters of complexes II seem independent of M and M', but slightly dependent on the nature of L-L and R. Changes in L-L and R would be expected to change both the electronegativity and size of the orbitals on M, the latter being, presumably, directly related to the magnitude of the repulsive forces between M and M'. Since the electronegativity of M and the repulsive forces between M and M' may be connected in this way, it is not possible to say whether repulsive forces are significant, and, if they are significant, how much they contribute to the overall lowering of the carbonyl stretching frequencies and stretching parameters in complexes II as compared with complexes III.

The fact that the carbonyl stretching frequencies and stretching parameters are independent of M is rather surprising since, as was pointed out in Chapter 1, platinum seems more electronegative than palladium in $(L\text{-}L)M(SMe)_2$. This may possibly indicate that the difference in

electronegativity between Pd and Pt is too small to have an effect on the carbonyl groups on M', or that the electronegativities of Pd and Pt in $(L\text{-}L)M(SMe)_2$ are modified slightly differently when $(L\text{-}L)M(SMe)_2$ is complexes onto a Group VI metal. This may account for the small differences observed in the electronic spectra of complexes II ($L\text{-}L = Ph_2PCH_2CH_2PPh_2$; $M = Pt$; $R = Me$) as compared with the spectrum of $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$.

It was postulated in Chapter 1, that the vacant orbital on M in $(L\text{-}L)M(SR)_2$ will approximate to a p_z orbital in the co-ordinate axes of Figure 2.9. Since there is a vacant orbital on M, there is a theoretical possibility of an M'⟶M bond being formed. Inspection of the available orbitals on M' shows that this M'⟶M bond would have to be a $d_{(xz)} \rightarrow p_z$ π-bond, unsupported by any σ-bond, as shown in Figure 2.9.

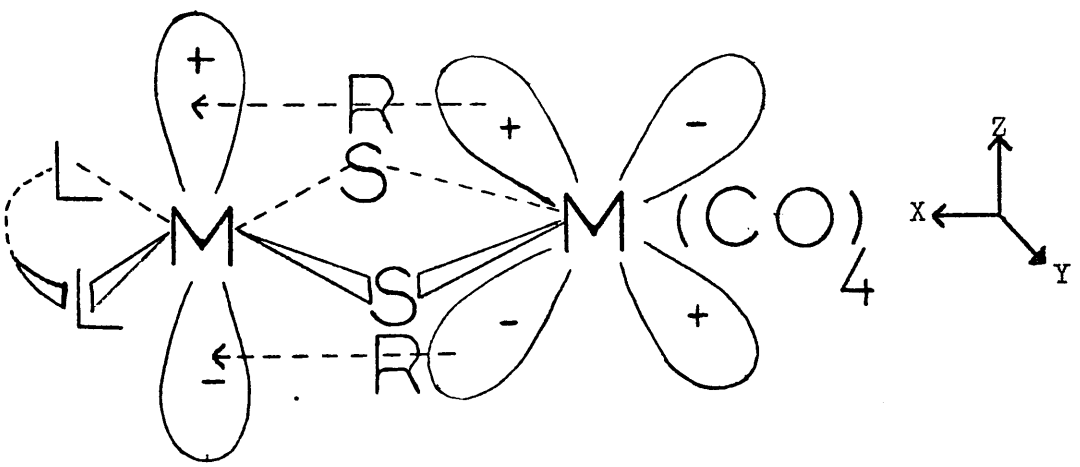
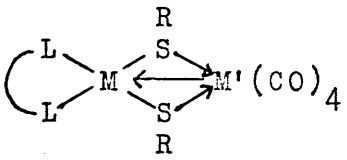


Figure 2.9 Theoretical M'⟶M bond in complexes II.

There is, however, no evidence to suggest that such a bond exests, or more precisely, if such a bond exists, it must be very weak as compared with the M'-Ti bond in complexes I, since the spectroscopic evidence for a metal-metal bond in complexes I is completely absent in the spectra of complexes II. Therefore, a formulation such as IIb can almost certainly be ruled out.



IIb

Metal-metal π-bonds are not completely unknown in organometallic chemistry, but they are rather rare. Nesmeyanov[86] has postulated the presence of an Nb-Nbπ-bond in $\left[CpNb(CO)Ph_2C_2\right]_2$ to account for the short Nb-Nb bonding distance as compared with that observed in αNbI_4[87]. This postulated Nb-Nb π-bond is, however, supported by a σ-bond; unsupported π-bonds are unknown.

CHAPTER 3

The Complexes $(Cp_2Ti[SR]_2CuX)_n$

From their analytical figures, the complexes formed by the reaction of $Cp_2Ti(SR)_2$ (R = Me, Ph) with $(1,5\underline{cyclo\text{-}octadiene}\text{-}CuX)_2$ (X = Cl, Br) have the empirical formula $Cp_2Ti[SR]_2CuX$, IV. When these complexes were reacted with phosphines, $Cp_2Ti(SR)_2$ was liberated, suggesting that $Cp_2Ti(SR)_2$ remains intact in complexes IV.

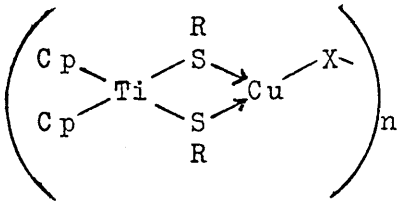
Complexes of empirical formula $RSCH_2CH_2SRCuX$, V, (R = Me, Ph; X = Cl, Br) were prepared by the reaction of CuX_2 and $RSCH_2CH_2SR$ in the presence of triphenyl phosphite, which acts as a reducing agent[88]. The same complexes (V) could not, however, be prepared from the reaction of $(1,5\underline{cyclo\text{-}octadiene}\text{-}CuX)_2$ with $RSCH_2CH_2SR$.

It has been found that the complexes (di-olefinCuX) differ markedly in their molecular structure depending on

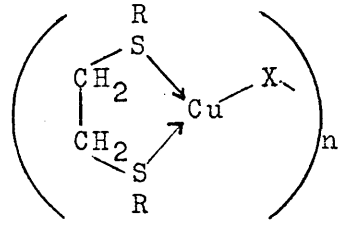
the di-olefin used, e.g. 1,5cyclo-octadiene-CuCl, norbornadiene-CuCl, and cyclo-octatetraene-CuCl have been found to exist as a dimer[89], a tetramer[90], and a polymer[91], respectively.

The complexes of empirical formulae $Cp_2Ti[SR]_2CuX$ and $RSCH_2CH_2SRCuX$ therefore probably exist in the forms $(Cp_2Ti[SR]_2CuX)_n$ and $(RSCH_2CH_2SRCuX)_n$ where n is greater than 1. However, it is not possible to say, since molecular weights could not be obtained, whether n has the same value in IV and V, or whether n varies in each set depending on the nature of R and X.

It will be assumed that both $Cp_2Ti(SR)_2$ and $RSCH_2CH_2SR$ behave as chelating ligands, so that the copper containing complexes have the forms IVa and Va



IVa



Va

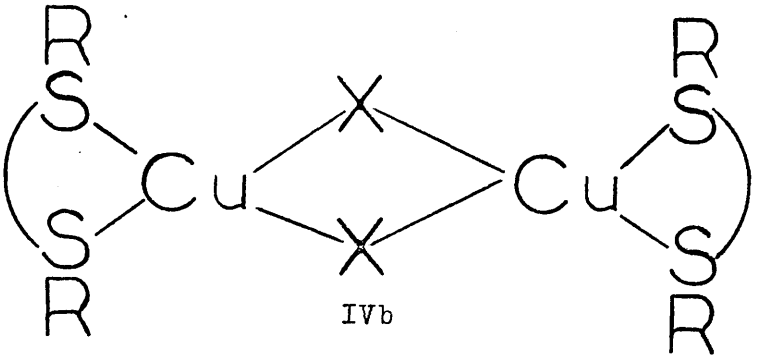
Further, since complexes IV (R = Me) were formed very readily from $(1,5\text{cyclo-octadiene-CuX})_2$, which is known[89] to exist as a dimer, in the solid state at least, it is suggested that in complexes IV (R = Me), n = 2.

The failure to prepare complexes V from $(1,5\underline{\text{cyclo-octadiene}}\text{-CuX})_2$, suggests that in complexes V, n may be greater than 2.

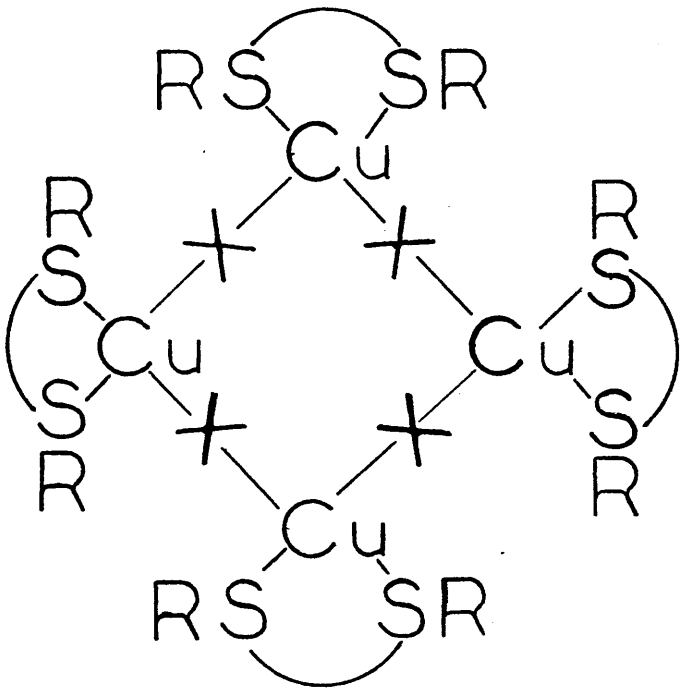
The preparation of complexes IV (R = Ph) via $(1,5\underline{\text{cyclo-octadiene}}\text{-CuX})_2$ did not go as readily as when R = Me, so that the value of n in IV (R = Ph) is in some doubt. Although it was found (Chapter 2) that in the preparations of complexes I and II the reactions, with a given Group VI metal, were slower when R = Ph than when R = Me, in the reactions of $Cp_2Ti(SPh)_2$ with $(1,5\underline{\text{cyclo-octadiene}}\text{-CuX})_2$ there may well be time for isomerisation of the latter to take place leading to a form other than a dimer being present as the reactive species.

If n = 2, complexes IV and V will have structures similar to IVb (Figure 3.1), whereas if n is greater than 2, structures similar to IVc and IVd are to be expected. (In Figure 3.1, the "ligand" RS⌒SR represents both $RSCH_2CH_2SR$ and $Cp_2Ti(SR)_2$).

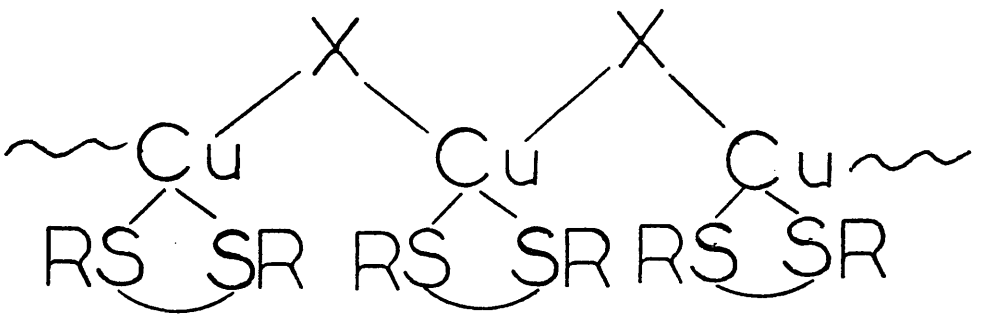
As the complexes IV are highly insoluble, only those techniques which can be applied to solids could be used to investigate the properties of these complexes. The three techniques used were, X-ray powder photography,



IVb



IVc



IVd

Figure 3.1 Possible structures of the complexes $(Cp_2Ti[SR]_2CuX)_n$. n = 2,4, and a large number in IVb, IVc, and IVd respectively.

diffuse reflectance electronic (14,000-30,000cm.$^{-1}$) spectroscopy, and far infra-red (40-400cm.$^{-1}$) spectroscopy. The information obtained from the first two of these techniques will be discussed here, but the far infra-red spectra will be considered, with similar data for all the heteronuclear complexes prepared, in the following chapter.

The powder photographs of $(Cp_2Ti[SMe]_2CuCl)_n$ and $(Cp_2Ti[SMe]_2CuBr)_n$ are very similar, suggesting that $\underline{n}$ may have the same value in each complex: the value of $\underline{n}$ is thought to be 2, for the reason already mentioned above. The powder photographs of the phenyl analogues are similar to each other, but differ noticeably from those of the methyl complexes, suggesting that in $(Cp_2Ti[SPh]_2CuCl)_n$ and $(Cp_2Ti[SPh]_2CuBr)_n$ the value of $\underline{n}$ is the same, although its value may differ from that in the analogous methyl complexes. Little emphasis can, however, be placed on these results, as they only give information about crystal, rather than molecular structures.

The bands observed in the diffuse reflectance electronic spectra of complexes IV, together with those bands observed in the spectra of $Cp_2Ti(SR)_2$ are listed in Table 3.1. Typical spectra of complexes IV are shown in Figure 3.2.

Table 3.1

Bands observed in the electronic spectra of complexes IV.

Complex	Observed bands ($cm.^{-1}$)
$Cp_2Ti(SMe)_2$	26600 19000
$Cp_2Ti(SPh)_2$	25000 18300
$(Cp_2Ti[SMe]_2CuCl)_2$	27700 20200 15300
$(Cp_2Ti[SMe]_2CuBr)_2$	27700 20200 15800
$(Cp_2Ti[SPh]_2CuCl)_n$	26300 21000 17300
$(Cp_2Ti[SPh]_2CuBr)_n$	26300 21700 17300

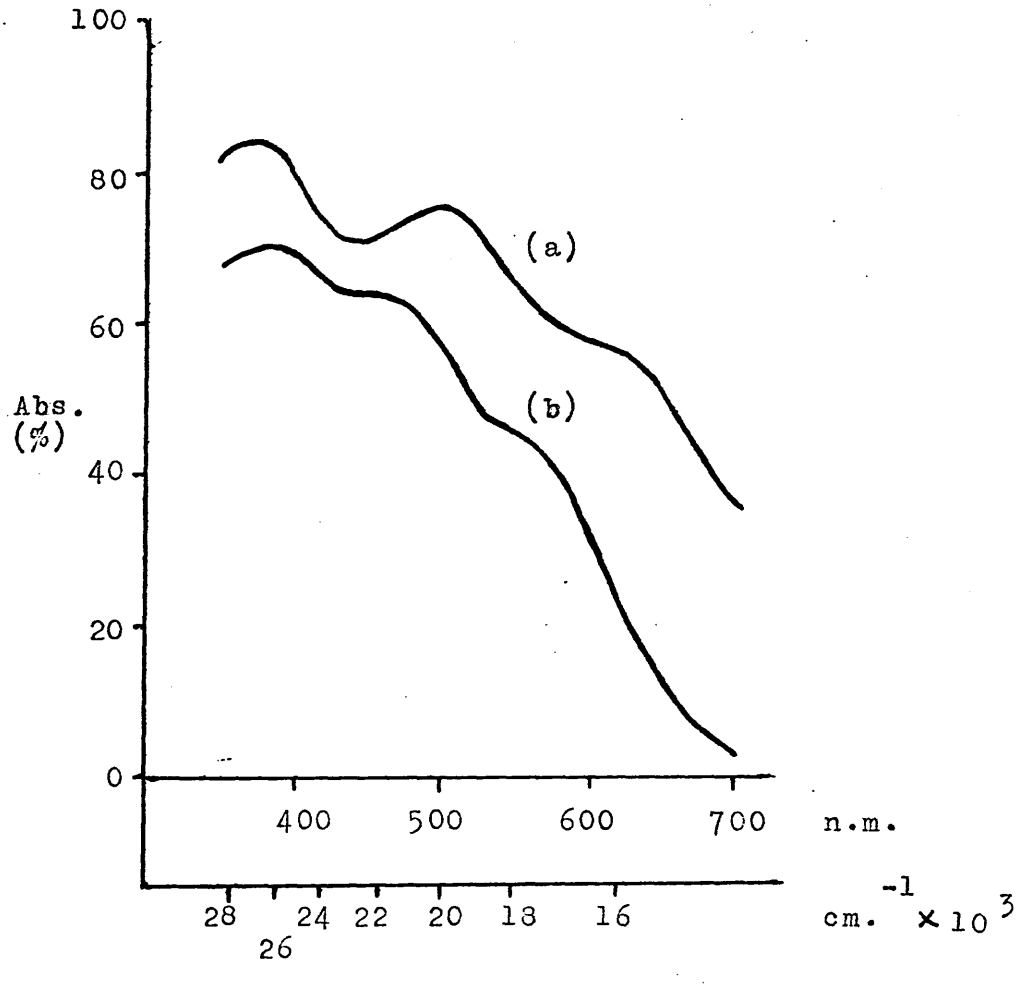
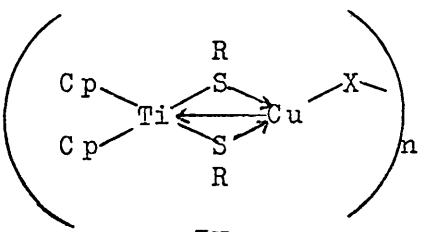


Figure 3.2 Diffuse reflectance electronic spectra of (a) $(Cp_2Ti[SMe]_2CuBr)_2$ and (b) $(Cp_2Ti[SPh]_2CuCl)_n$.

The most noticeable feature in the spectra of complexes IV, as compared with those of $Cp_2Ti(SR)_2$, is the appearance of a new band at 17,300cm.$^{-1}$ in $(Cp_2Ti[SPh]_2CuX)_n$ and at 15,300 and 15,800cm.$^{-1}$ in $(Cp_2Ti[SMe]_2CuX)_n$ with X = Cl and X = Br respectively.

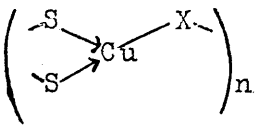
The two high energy bands at 20,000cm.$^{-1}$ and 27,000cm.$^{-1}$ (approx.) are assigned to charge transfer to titanium from sulphur and the cyclopentadienyl rings, respectively, by analogy with the solution spectra of $Cp_2Ti(SR)_2$. (See Chapter 1).

The new band in complexes IV is thought to arise from a transition involving both metals, in much the same way as was suggested for complexes I. (See Chapter 2). In complexes IV, a Cu→Ti charge transfer, as in IVe, is postulated.



IVe

Depending on the value of n, the molecular structure of complexes IV will vary, but, considering only one TiSCuS ring at a time, the symmetry around Ti is similar to that in $Cp_2Ti(SR)_2$, so that the new band is not thought

to arise from a weak band in $Cp_2Ti(SR)_2$ which gains in intensity on complexation. The band is not thought to be associated with any transitions involving the  system since complexes V are white. On the other hand, since the extinction coefficients of the bands are unknown, the relative intensities of the bands are unknown and it is not possible to assign this new band completely unambiguously.

Unlike the corresponding spectra of complexes I, the high energy peaks in $Cp_2Ti(SR)_2$ have moved to even higher energy on formation of complexes IV. The increased energy required for these transitions to take place is to be expected if the copper atom is now pushing electrons onto titanium, as in IVe, making the titanium atom less electrophilic. These observations would seem to indicate that the charge transfer from sulphur and from the cyclopentadienyl rings is influenced by charge transfer from copper to titanium. This seems rather more clear cut than in complexes I, where there does not seem to be any correlation between charge transfer from the rings to titanium and from M' to titanium. (See Chapter 2).

Because of the presence of such a charge transfer band, the existence of a Cu→Ti dative bond is postulated.

By choosing a suitable hybridisation scheme for the orbitals on copper and titanium, a suitable filled copper orbital can overlap with the vacant orbital on titanium forming a Cu→Ti bond exactly analogous to the M'→Ti bond postulated in complexes I.

CHAPTER 4

The Far Infra-Red Spectra (400-40cm.$^{-1}$) of Multi-Heteronuclear Complexes.

This chapter will be concerned with the far infra-red spectra (400-40cm.$^{-1}$) of the multi-heteronuclear complexes prepared. Each of these complexes has an MBM'B ring (B is a bridging ligand and M and M' are transition metals) which may or may not have an M-M' bond. The assignments which have been made are, for the main part, those associated with M-B and M'-B stretching and bending modes in this 4 membered ring.

Before considering the individual spectra in detail, it will be necessary to describe the basis on which the various assignments, associated with the vibrations of the M-B and M'-B bonds, have been made. As an example, it will be instructive to consider one of the complexes discussed in Chapter 2, $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$ (A), which has a TiSMoS 4 membered ring.

An attempt has recently been made[92] to work out the detailed vibrations expected in homodinuclear bridged complexes, but the results are not applicable to the complexes prepared in this present research since these are heteronuclear species. Also, the assignments made in the literature report[92] are based on unambiguous assignments from model systems.

In the complexes $Cp_2Ti(SMe)_2$ and $MeSCH_2CH_2SMeMo(CO)_4$ the methylene and/or methyl groups attached to sulphur are light as compared with sulphur, and the C-S stretching frequency is much higher than that of the Ti-S and the Mo-S stretching vibrations, hence symmetric and asymmetric Ti-S and Mo-S stretching vibrations can exist in these complexes. However, in A this approximation does not hold since the two metal atoms, or more exactly, the Cp_2Ti and $Mo(CO)_4$ groups are heavy as compared with sulphur. Therefore, pure Ti-S and Mo-S stretching vibrations cannot

exist since the S-methyl groups are restricted in their motion relative to Ti and Mo by being "anchored" to the heavy $Mo(CO)_4$ and Cp_2Ti groups, respectively.

One way of looking at A is to consider the two heavy groups, Cp_2Ti and $Mo(CO)_4$, as being fixed, leaving the S-methyl groups free to vibrate in between. In this way the vibrations of the S-methyl groups, as a whole, can be divided into two classes: those which are in the plane of the ring, and those which are perpendicular to it. Vibrations of the S-methyl group in the plane of the ring can be looked upon as being compounded from Ti-S and Mo-S stretching and bending modes, whereas those vibrations perpendicular to the ring are made up of Ti-S and Mo-S bending and twisting modes. For the purposes of this discussion, only those vibrations of the S-methyl groups in the plane of the ring will be considered. The out of plane vibrations which contain considerable amounts of bending and twisting modes will probably come at very low frequencies.

In the plane of the ring each of the S-methyl groups, as a whole, will have 2 degrees of freedom, hence 4 possible vibrational modes of these groups are expected. Neglecting the methyl groups attached to sulphur, the TiSMoS ring in A has C_{2v} symmetry with the C_2 axis along

the line joining the two metal atoms. The individual movements described by each of the sulphur atoms in any of the possible vibrational modes must transform among themselves under the elements of C_{2v} symmetry. Thus, movements of the sulphur atoms as in Ia (Figure 4.1) do not constitute a fundamental vibration, but those movements of the sulphur atoms as in Ib,Ic,Id, and Ie (Figure 4.1) do constitute fundemental modes. These vibrations transform under C_{2v} as shown in Figure 4.1 and, as there will be strong coupling between those vibrations of the same symmetry species, i.e. there will be coupling between Ib and Ic and between Id and Ie, vibrational modes such as If,Ig,Ih, and Ii are to be expected.

The prerequisite for infra-red activity is an oscillating dipole, and the size of the dipole governs the intensity of the peak observed in the infra-red spectrum. Since each of the vibrational modes If-Ii gives rise to an oscillating dipole, as many as 4 peaks arising from simultaneous distortions of the Ti-S and Mo-S bonds can reasonably be expected in the far infra-red spectrum of A. The magnitude of the oscillating dipoles may differ in vibrational modes such as If-Ii and hence there are likely to be variations in the intensities of the observed peaks, and the possibility therefore arises that, of the 4 peaks

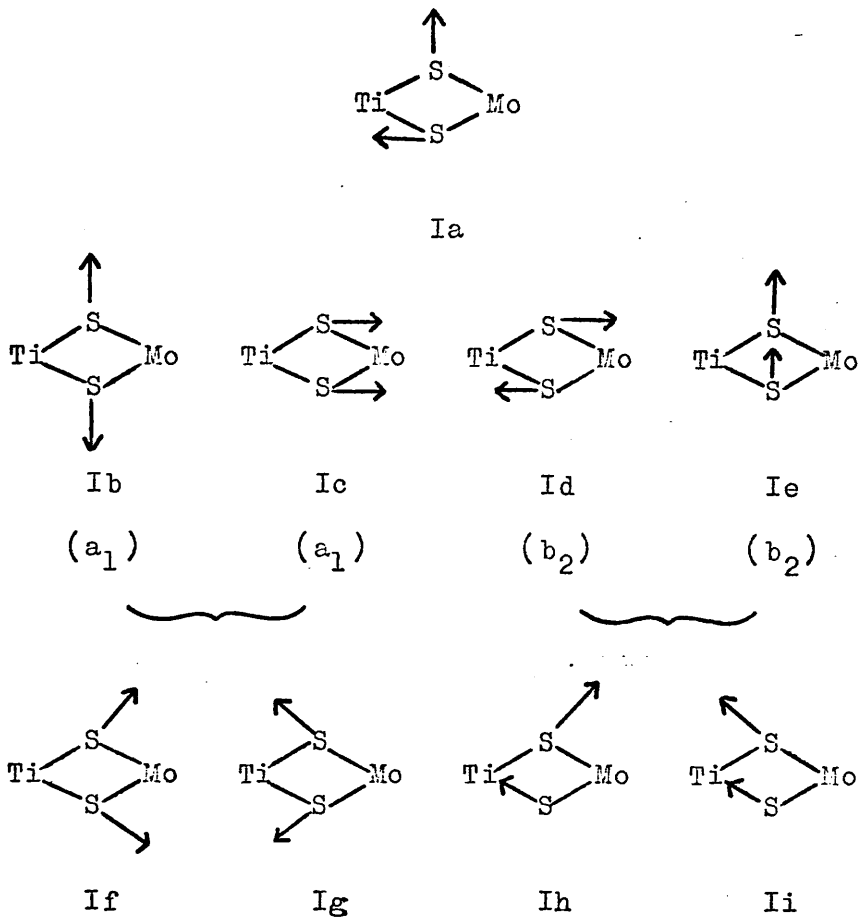


Figure 4.1 Possible vibrations in the TiSMoS ring in $Cp_2Ti[SMe]_2Mo(CO)_4$.

expected, some may be too weak to be observed. The expected peaks may also occur over a fairly wide range of frequencies depending on the relative amounts of bending and stretching modes which combine to produce the individual vibrations.

If the M-B and the M'-B bonds in the MBM'B ring are of comparable strength then the vibrations that have already been described are to be expected. If, however, the M-B bonds are very much stronger than the M'-B bonds then the vibrations in the MBM'B ring are expected to approximate to pure vibrations of the M-B bonds. In other words, the spectrum of a complex such as $(L)_x M\begin{smallmatrix} B \\ \diagup \quad \diagdown \\ B \end{smallmatrix} M'(L)_y$ in which the M'-B bonds are very weak, will be similar to that of the mononuclear complex $(L)_x M\begin{smallmatrix} B \\ \diagdown \\ B \end{smallmatrix}$, as far as vibrations in the MBM'B ring are concerned. It should be pointed out that the M'-B bonds must be very weak as compared with the M-B bonds for the above hypothesis to be correct since an analogy might be drawn with hydrogen bonded species such as H-O---H, where a comparatively weak O---H bond considerably reduces the O-H stretching frequency.

Certain experimental difficulties were encountered in recording some of the spectra. The fine, powdery form of some of the complexes rendered them highly electrostatic, and when "Rigidex" discs were made up, the complexes tended

to concentrate on the periphery of the disc, leaving a very low concentration of the complexes in the centre of the disc, which is, of course, the part illuminated by the beam. This resulted in very weak peaks in the spectra, and the peaks could not, in some cases, be distinguished from the background noise.

In view of the assumptions made as to the number and intensities of the peaks to be expected in complexes containing an MBM'B ring, all the assignments are of a very tentative nature.

1) The complexes $Cp_2Ti[SR]_2M'(CO)_4$ (R = Me, Ph; M' = Mo, W).

Attempts[93] to assign the peaks in the far infra-red spectrum of Cp_2TiCl_2 have met with little success. Comparison of the spectra of Cp_2TiCl_2 (Figure 4.2) and $Cp_2Ti(SMe)_2$ (Figure 4.3) shows that they have an overall similarity except that the peaks at 246 and 276cm.$^{-1}$ in Cp_2TiCl_2 are replaced by a single peak at 280cm.$^{-1}$ in $Cp_2Ti(SMe)_2$, and whereas 2 peaks at 360 and 405cm.$^{-1}$ are found in Cp_2TiCl_2, in $Cp_2Ti(SMe)_2$ peaks at 365 and 392cm.$^{-1}$ are observed. The peaks at 365 and 392cm.$^{-1}$ in $Cp_2Ti(SMe)_2$ are assigned to Ti-S stretching modes. These are in approximate agreement with reported[94] Ti-S stretching frequencies in $(NMe_2)_2Ti(SEt)_2$ and $(NMe_2)_3Ti(SEt)$. The

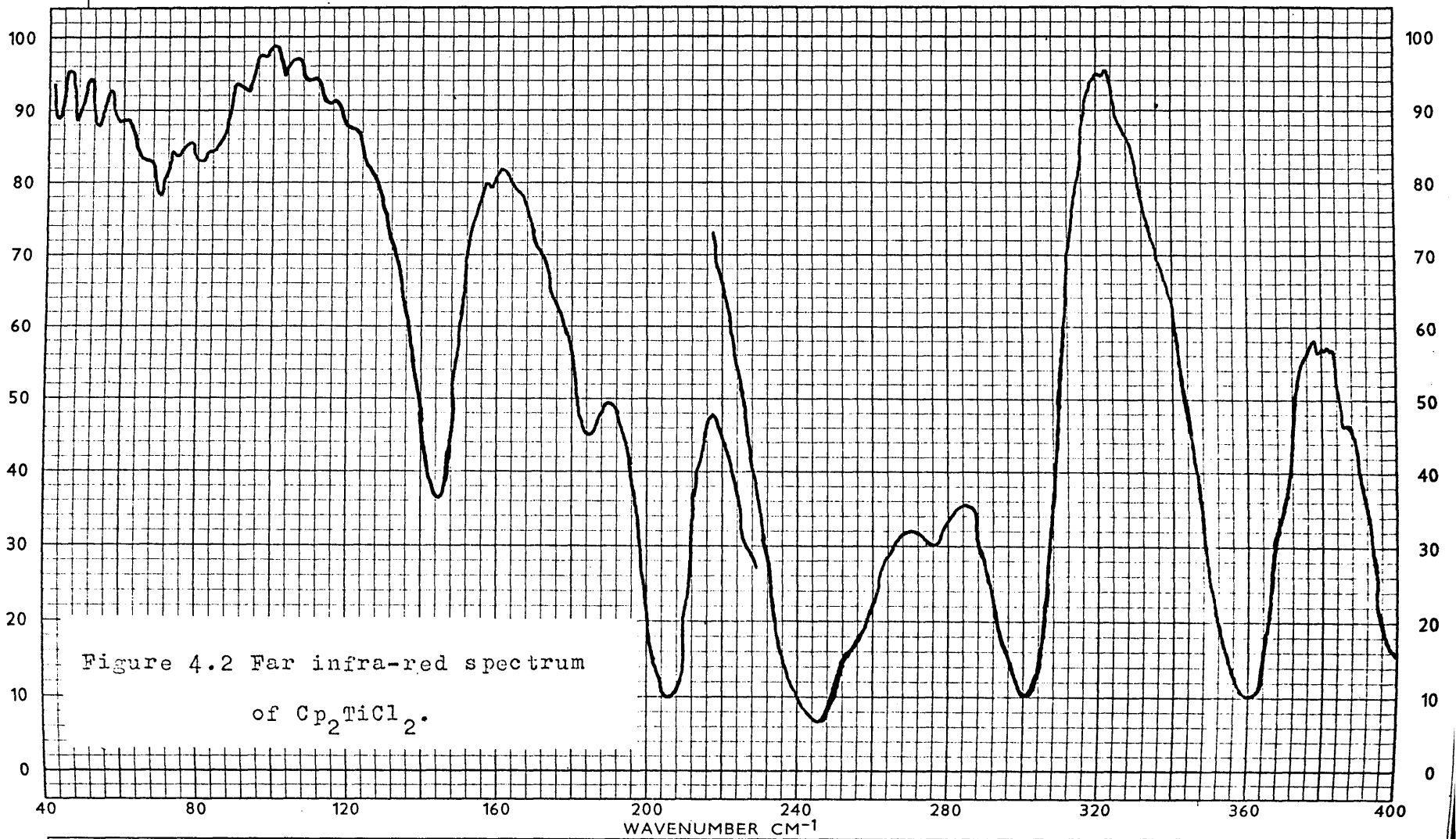


Figure 4.2 Far infra-red spectrum of Cp_2TiCl_2.

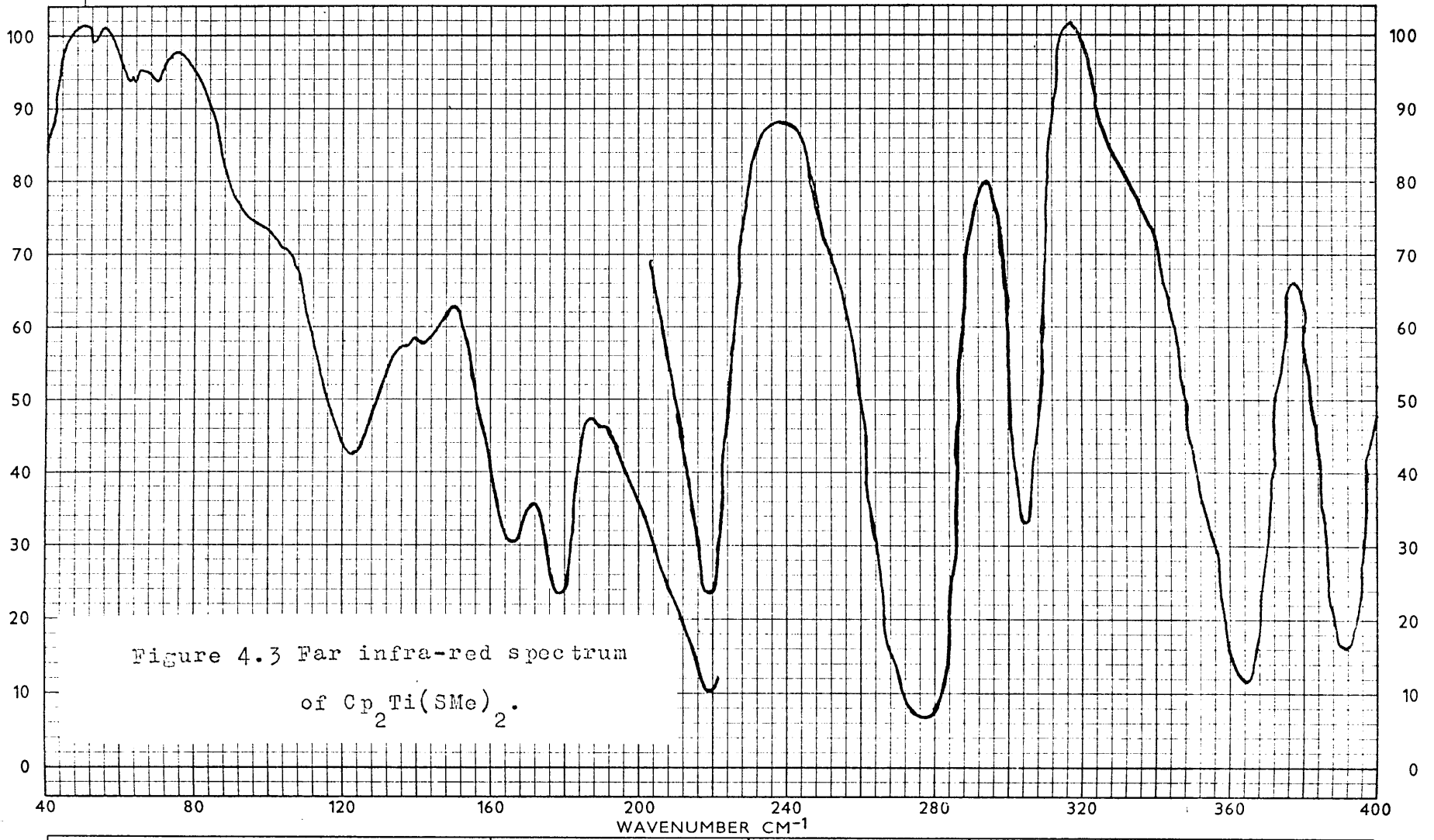


Figure 4.3 Far infra-red spectrum of $Cp_2Ti(SMe)_2$.

peaks at 280 and 305cm.$^{-1}$ in $Cp_2Ti(SMe)_2$ are thought to be due to Ti-cyclopentadienyl ring vibrations.

The spectrum of $Cp_2Ti(SPh)_2$ (Figure 4.4) shows rather broad peaks at 264 and 307cm.$^{-1}$ which can be equated with those associated with the Ti-ring vibrations at 280 and 305cm.$^{-1}$ in $Cp_2Ti(SMe)_2$. Peaks at 330,340,358, and 380cm.$^{-1}$ may arise from stretching vibrations of the Ti-S-Ph moieties. The vibrations of the Ti-S-Ph moieties would probably be expected to be more complicated than those of the Ti-S-Me sequence since there are low energy vibrations of the phenyl ring in the former which may well combine with the Ti-S stretching vibrations. (Compare the spectrum of $PhSCH_2CH_2SPh$, Figure 4.5).

Broad peaks in the spectrum of $MeSCH_2CH_2SMeW(CO)_4$ (Figure 4.6) at 95-120cm.$^{-1}$ and at 384cm.$^{-1}$ must be assigned to C-W-C bending and W-C stretching vibrations, respectively, as described by Jones[95a] and Lewis[95b]. The weak peaks at 284 and 304cm.$^{-1}$ in $MeSCH_2CH_2SMeW(CO)_4$ can therefore be assigned to W-S stretching vibrations. The corresponding spectrum of $MeSCH_2CH_2SMeMo(CO)_4$ was not obtained because of the experimental difficulties mentioned above.

The main feature of the spectra of complexes I (Figures 4.7-4.10) is the large increase in the number

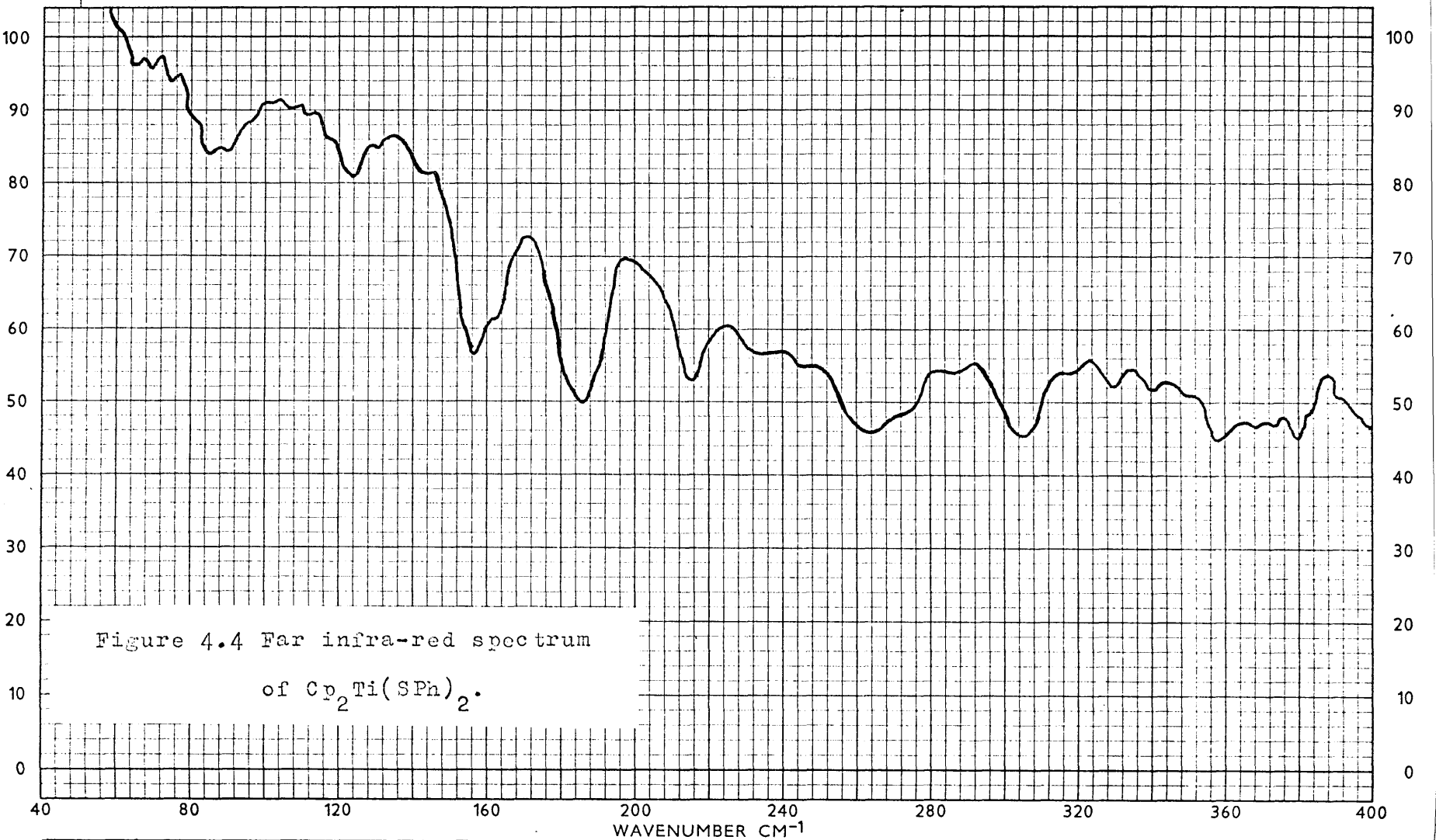


Figure 4.4 Far infra-red spectrum of $Cp_2Ti(SPh)_2$.

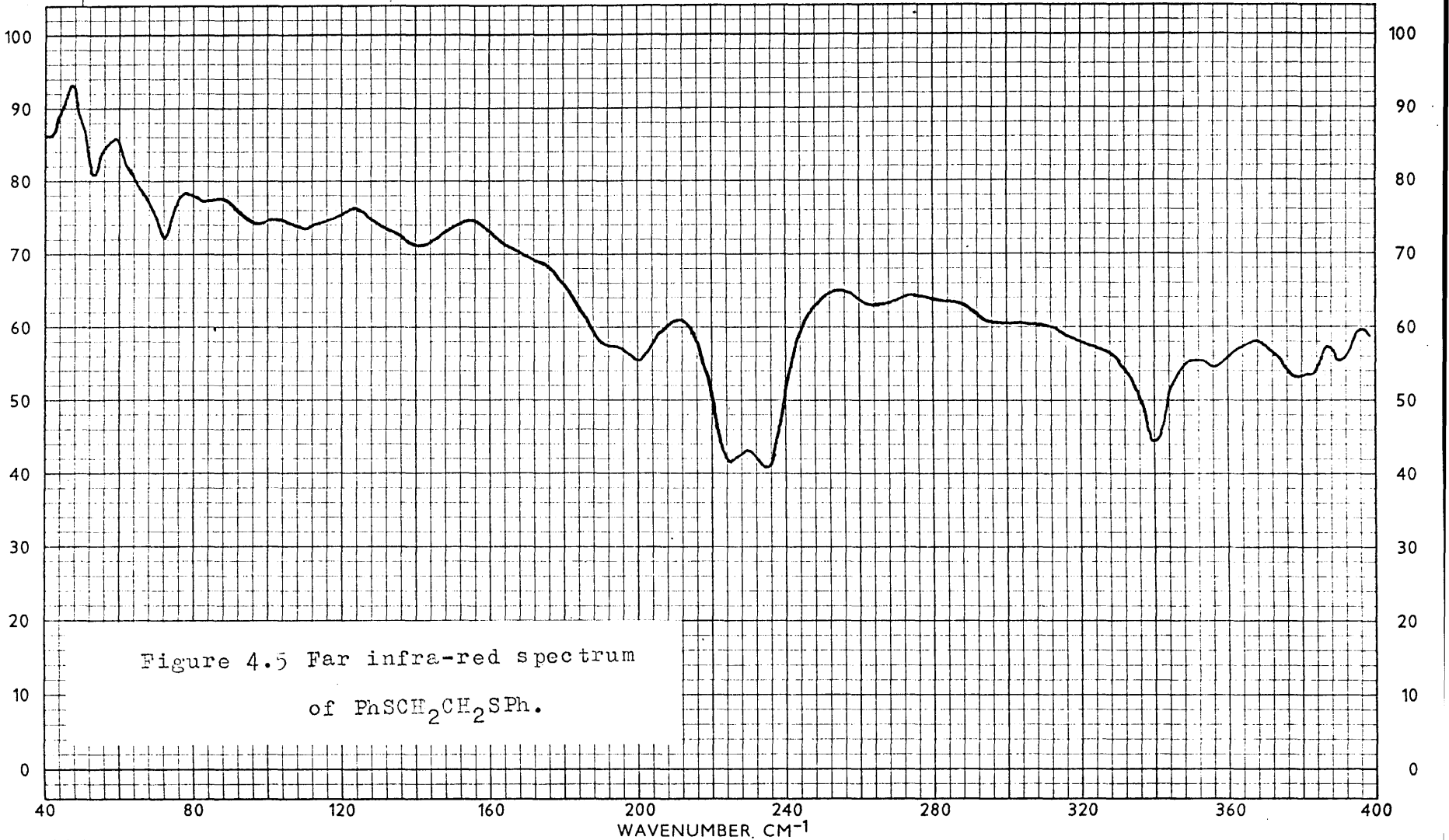


Figure 4.5 Far infra-red spectrum of $PhSCH_2CH_2SPh$.

Sample	Sampling interval 8	Amplifier	Wave Analyser	Date
	Beam Splitter	Coarse Gain	Bgd. Attenuation	

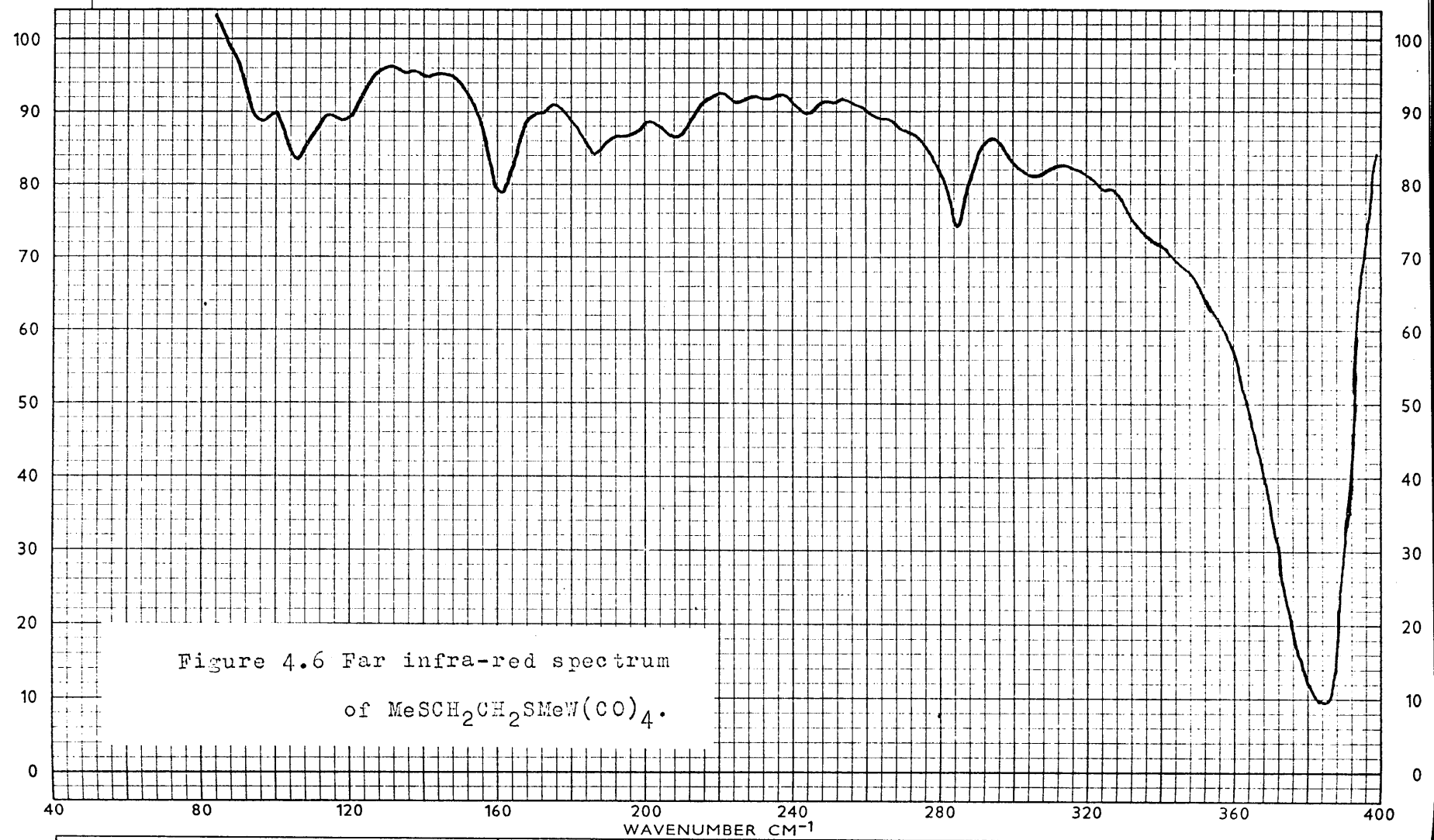


Figure 4.6 Far infra-red spectrum of $MeSCH_2CH_2SMeW(CO)_4$.

of peaks in the region 280-400cm.$^{-1}$, as compared with $Cp_2Ti(SR)_2$, even allowing for the presence of peaks arising from W-C stretching vibrations as are observed in $MeSCH_2CH_2SMeW(CO)_4$. This increase in the number of peaks is particularly noticeable when the spectrum of $Cp_2Ti(SMe)_2$ is compared with that of $Cp_2Ti\left[SMe\right]_2W(CO)_4$. All the spectra of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$ were of rather poorer quality than those of the corresponding tungsten complex, but the asymmetry on the low energy side of the highest energy peak suggests the presence of more peaks in the region 300-365cm.$^{-1}$ in the spectrum of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$. The overall similarity of the spectra of $Cp_2Ti(SMe)_2$ and $Cp_2Ti\left[SMe\right]_2W(CO)_4$ below 280cm.$^{-1}$, apart from the peak at 92cm.$^{-1}$ in the latter, which can be assigned to C-W-C bending vibrations, indicates that if any peaks arising from simultaneous distortions of the Ti-S and W-S bonds occur, they must be in the range 280-400cm.$^{-1}$.

Removal of the peaks at 368,376, and 382cm.$^{-1}$ as being due to W-C stretching vibrations, leaves peaks at 296,317, 324, and 345cm.$^{-1}$ which are not present in the spectrum of $Cp_2Ti(SMe)_2$, although the peak at 305cm.$^{-1}$, present in $Cp_2Ti(SMe)_2$, is absent from the spectrum of $Cp_2Ti\left[SMe\right]_2W(CO)_4$. This last mentioned peak may be equated with the sharp, though relatively weak peak at 296cm.$^{-1}$ in spectrum of $Cp_2Ti\left[SMe\right]_2W(CO)_4$

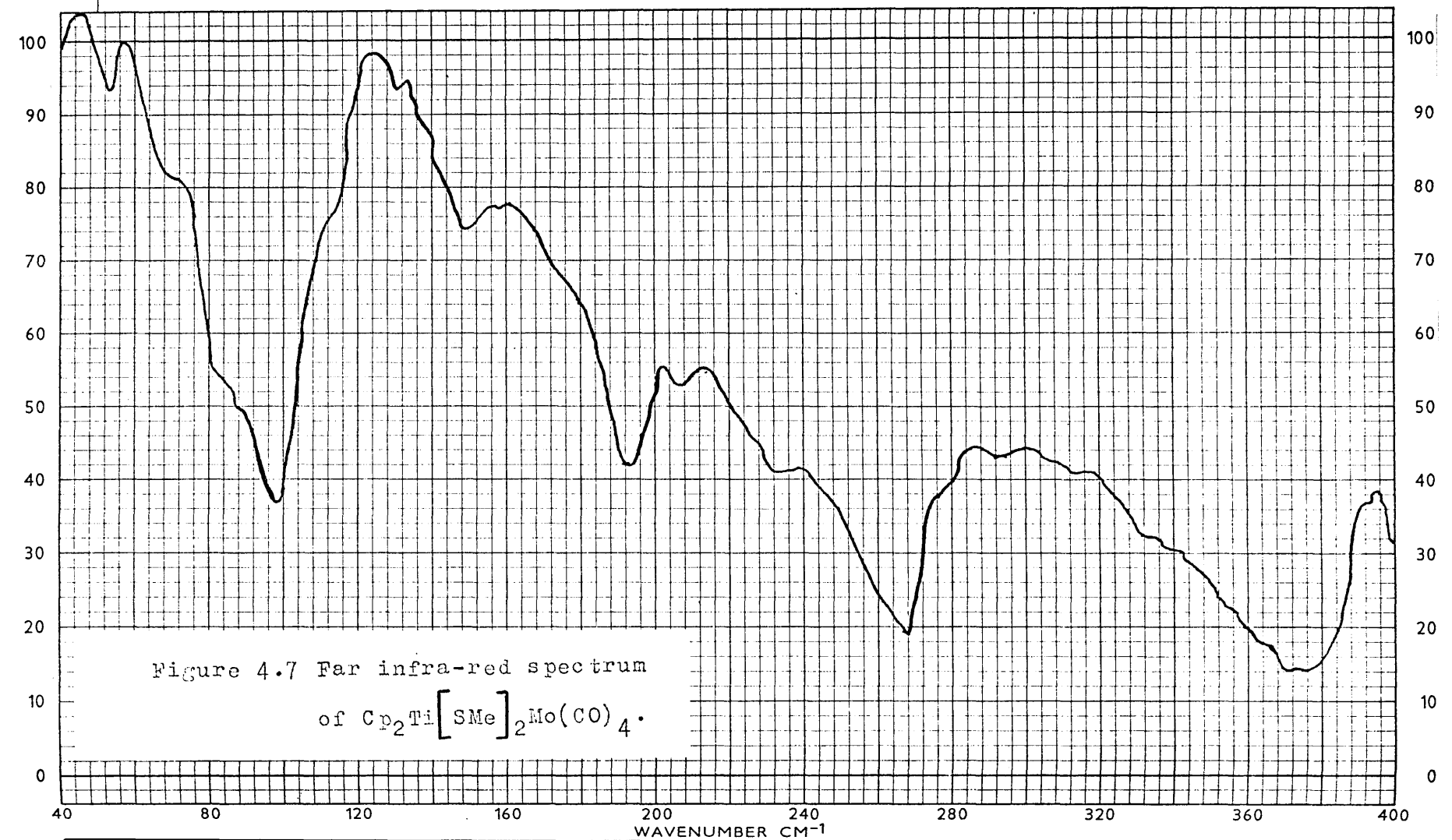


Figure 4.7 Far infra-red spectrum of $Cp_2Ti[SMe]_2Mo(CO)_4$.

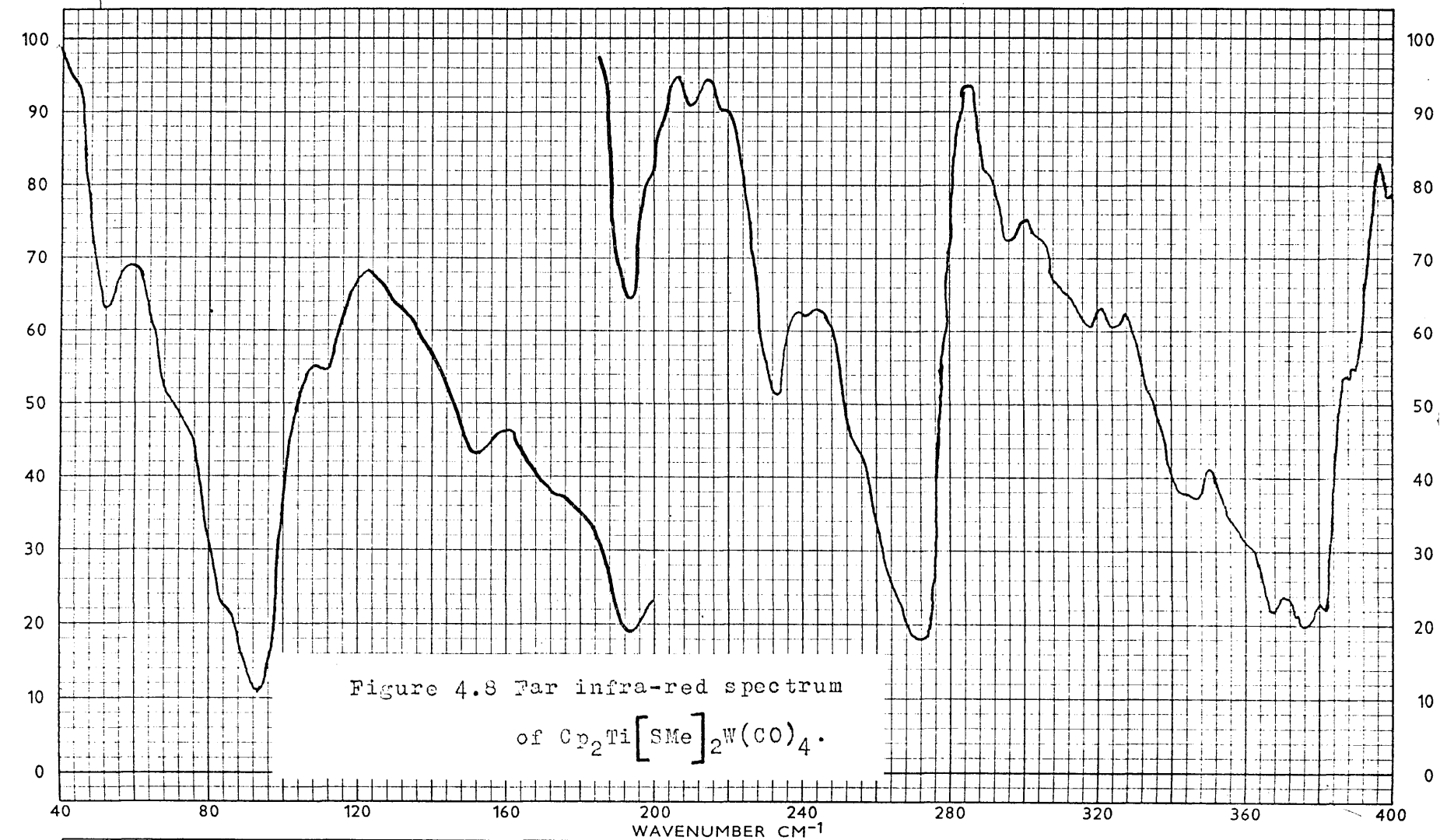


Figure 4.8 Far infra-red spectrum of $Cp_2Ti[SMe]_2W(CO)_4$.

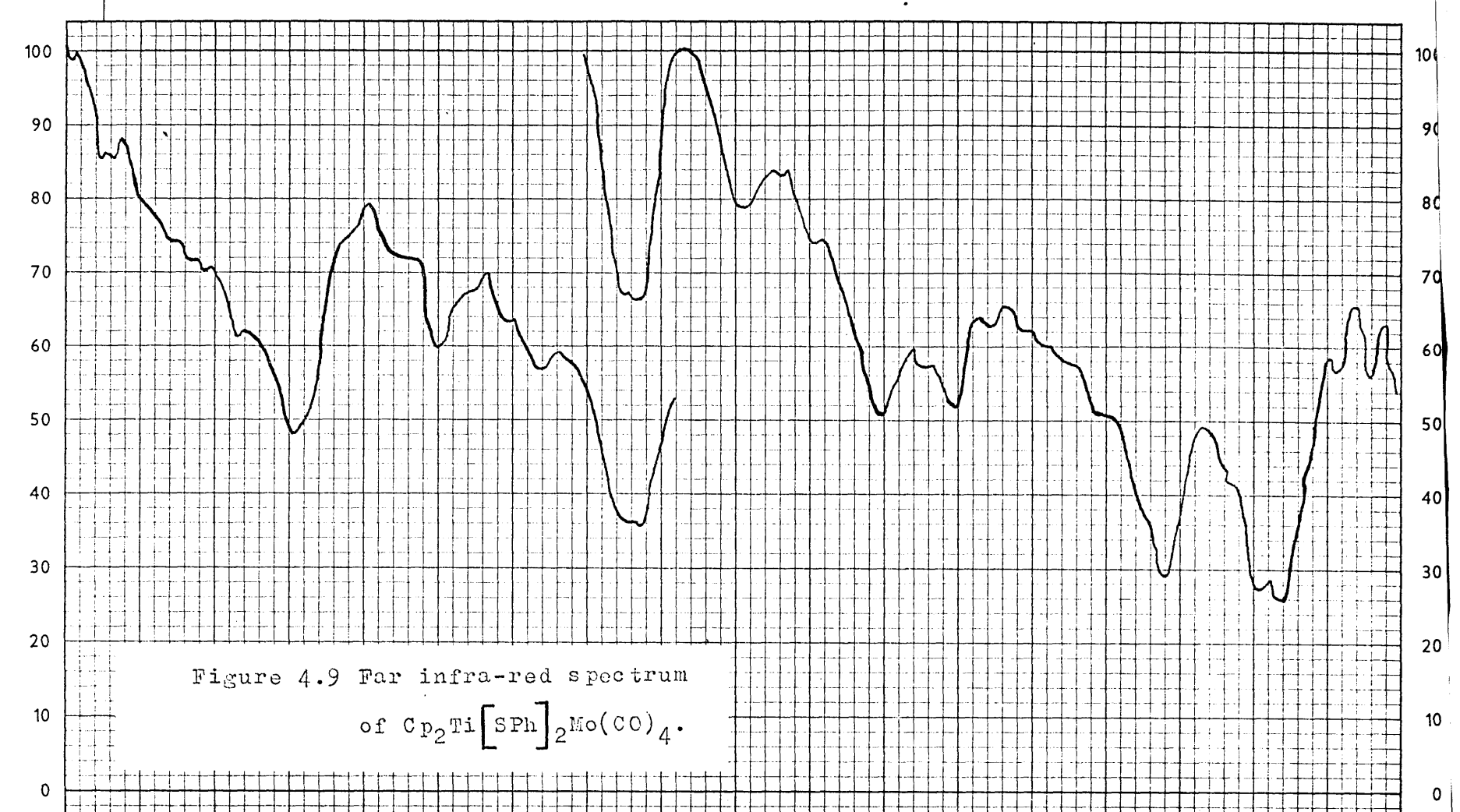


Figure 4.9 Far infra-red spectrum of $Cp_2Ti[SPh]_2Mo(CO)_4$.

Figure 4.10 Far infra-red spectrum of $Cp_2Ti[SPh]_2W(CO)_4$.

The peaks which remain, i.e. those at 317, 324, and 345cm.$^{-1}$, are therefore assigned to vibrations arising from simultaneous distortions of the Ti-S and W-S bonds in the TiSWS ring. Although similar peaks cannot be located accurately in the spectrum of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$, it is inferred from the asymmetry of the highest energy peak, that such peaks are present between 300 and 360cm.$^{-1}$.

The spectra of $MeSCH_2CH_2SMeCr(CO)_4$ and $Cp_2Ti\left[SMe\right]_2Cr(CO)_4$ which were obtained were of very poor quality and have therefore been left out of the above discussion.

The differences in the spectra of $Cp_2Ti(SPh)_2$ and of complexes I (R = Ph) (Figures 4.9 and 4.10) lie in the range 220-400cm.$^{-1}$ which, unlike the differences in the spectra of the methyl analogues, covers the Ti-cyclopentadienyl ring vibrations. This suggests that in complexes I (R=Ph) the cyclopentadienyl rings are changed in some way as compared with the cyclopentadienyl rings in $Cp_2Ti(SPh)_2$ itself. The most probable explanation of this difference between methyl and phenyl derivatives is that there are steric interactions between the phenyl and cyclopentadienyl rings, whereas no such interactions occur with the smaller methyl groups. It should be remembered that there were differences observed in the carbonyl stretching frequencies of complexes I on changing a methyl

group for a phenyl group, so that these two observations may well be related.

The complex nature of the spectrum of $Cp_2Ti(SPh)_2$ in the range 300-400cm.$^{-1}$ added to the fact that there will be peaks arising from M'-C stretching vibrations in complexes I in this region, make assignments of the peaks arising from simultaneous distortions of the Ti-S and M'-S bonds very arbitrary. However, the peak at 338cm.$^{-1}$ in $Cp_2Ti\left[SPh\right]_2Mo(CO)_4$ and at 340cm.$^{-1}$ in $Cp_2Ti\left[SPh\right]_2W(CO)_4$ are tentatively assigned to such vibrations on the grounds that no strong peaks at these frequencies occur in the spectrum of $Cp_2Ti(SPh)_2$.

2) The complexes $Ph_2PCH_2CH_2PPh_2M\left[SMe\right]_2M'(CO)_4$ (M = Pd, Pt; M' = Mo, W).

Extreme experimental difficulties were encountered in recording the spectra of the complexes $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, II, because of the electrostatic phenomenon mentioned earlier. Of all the complexes II (See Chapter 2) only $Ph_2PCH_2CH_2PPh_2M\left[SMe\right]_2Mo(CO)_4$ (M = Pd, Pt) and $Ph_2PCH_2CH_2PPh_2Pt\left[SMe\right]_2W(CO)_4$ yielded spectra with peaks strong enough to distinguish between genuine peaks and background noise. The spectra which were obtained, were only satisfactory in the range 240-400cm.$^{-1}$. The recorded

spectra are shown in Figure 4.11, and those of $Ph_2PCH_2CH_2PPh_2M(SMe)_2$ (M = Pd, Pt) are shown in Figures 4.12 and 4.13.

The complex $Ph_2PCH_2CH_2PPh_2Pd[SMe]_2Mo(CO)_4$ shows 2 weak peaks at 288 and 298cm.$^{-1}$ and 2 stronger peaks at 320 and 374cm.$^{-1}$, the last mentioned having shoulders at 358, 364, and 349cm.$^{-1}$. The highest and lowest energy shoulders are probably the same peaks that occur in the spectrum of $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$ at 358 and 392cm.$^{-1}$. The strong peak at 374cm.$^{-1}$ and the weaker one at 364cm.$^{-1}$ are assigned to Mo-C stretching vibrations. Any two of the three remaining peaks at 288, 298, and 320cm.$^{-1}$ are sufficiently different in relative positions or intensities from those observed at 280, 307, and 320cm.$^{-1}$ in $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$ to assign them to something other than pure Pd-S stretching vibrations. (The peaks at 307 and 320cm.$^{-1}$ have already been assigned to Pd-S stretching vibrations, (See Table 1.1)). Thus the peaks at 288, 298, and 320cm.$^{-1}$ in $Ph_2PCH_2CH_2PPh_2Pd[SMe]_2Mo(CO)_4$ are thought to arise from simultaneous distortions of the Pd-S and Mo-S bonds in the PdSMoS ring.

Similarly, the peaks at 293, 309, and 324cm.$^{-1}$ in $PH_2PCH_2CH_2PPh_2Pt[SMe]_2Mo(CO)_4$ and at 291, 308, and 324cm.$^{-1}$ in $Ph_2PCH_2CH_2PPh_2Pt[SMe]_2W(CO)_4$ are thought to arise from

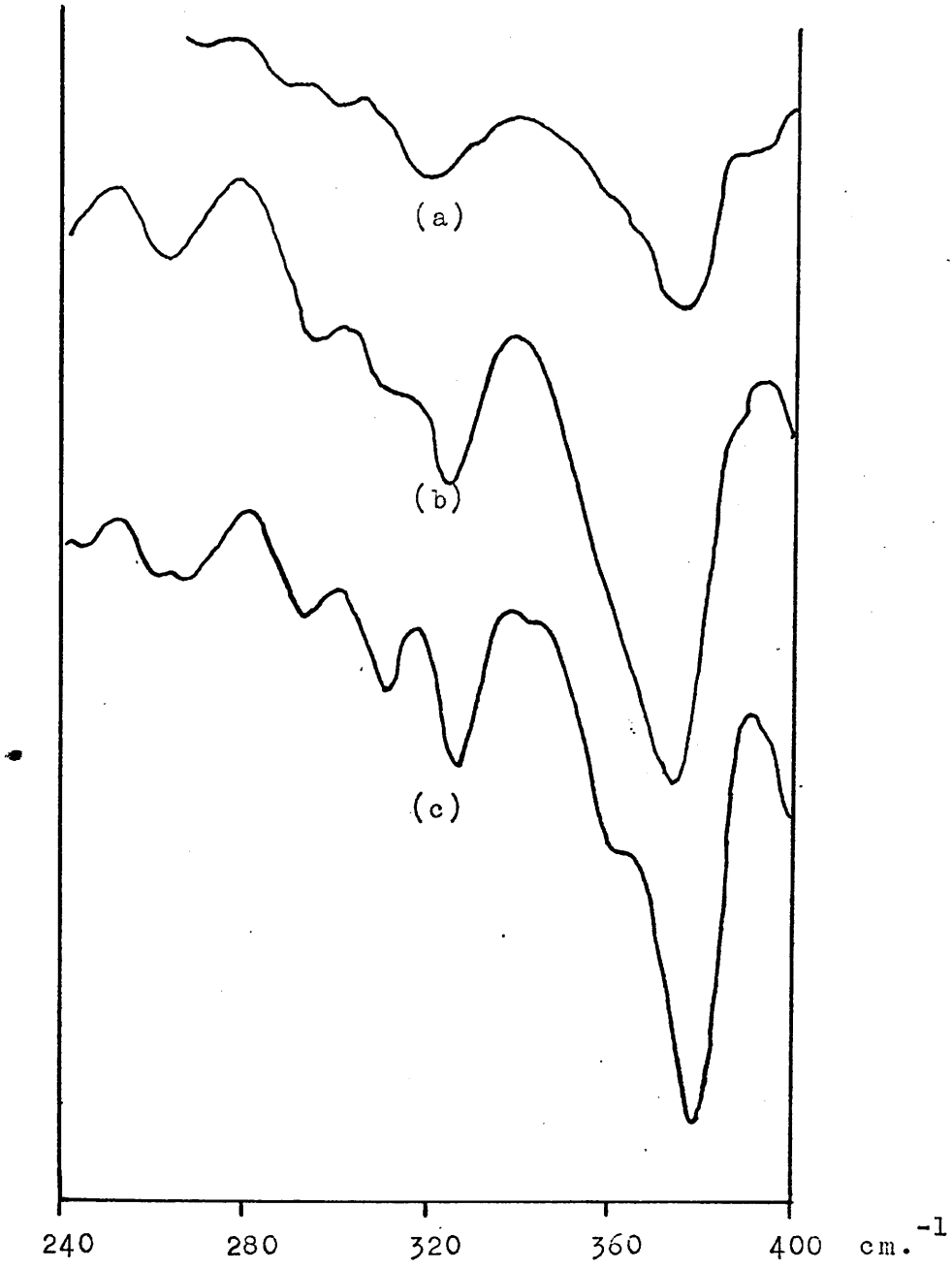


Figure 4.11 Far infra-red spectra of:-

(a) $Ph_2PCH_2CH_2PPh_2Pd[SMe]_2Mo(CO)_4$.

(b) $Ph_2PCH_2CH_2PPh_2Pt[SMe]_2Mo(CO)_4$.

(c) $Ph_2PCH_2CH_2PPh_2Pt[SMe]_2W(CO)_4$.

Figure 4.12 Far infra-red spectrum of $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$.

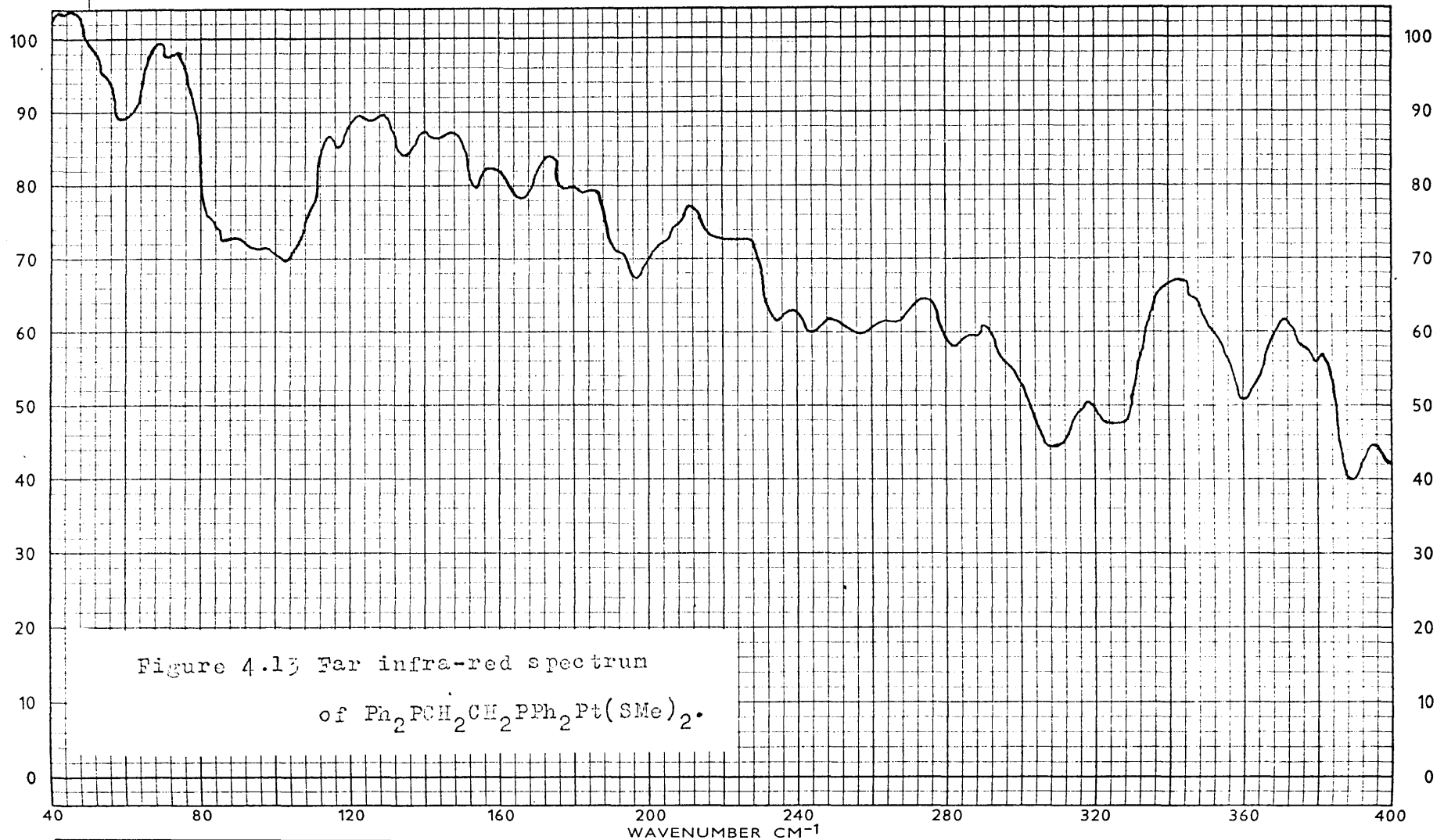


Figure 4.13 Far infra-red spectrum of $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$.

simultaneous distortions of the Pt-S and M'-S bonds in the PtSMoS and PtSWS rings.

On comparing the two sets of results for complexes I and II, it is found that in the former, the peaks assigned to simultaneous distortions of the Ti-S and M'-S bonds occur at frequencies between the pure Ti-S and M'-S stretching frequencies. The corresponding peaks in complexes II occur at the same frequencies as pure M-S and M'-S stretching vibrations. In this respect the two sets of results are consistent, but it is rather surprising that the vibrations arising from simultaneous distortions of the bonds in the central metal/sulphur 4 membered ring do not occur at lower frequencies since, as mentioned earlier, there will be a certain amount of bending of the bonds which will contribute to the overall vibration. This seemingly anomalous behaviour tends to contradict conclusions which have been reached elsewhere[96] concerning the relative energies of metal-terminal ligand and metal-bridging ligand vibrations in homodinuclear complexes. However, similar, apparently anomalous, behaviour has been reported[97] in homodinuclear complexes in which sulphur is again the bridge forming atom, so that the ability to form strong bridge bonds using its lone pairs may be a peculiar characteristic of sulphur.

3) The complexes $(Cp_2Ti[SR]_2CuX)_n$ (R = Me, Ph; X = Cl, Br).

If n varies in $(Cp_2Ti[SR]_2CuX)_n$, IV, and $(RSCH_2CH_2SRCuX)_n$, V, (See Chapter 3), the molecular structures of IV and V will be different, so that assignments of the peaks in the spectra of complexes IV based on peaks observed in the spectra of complexes V, are of a very tentative nature. Nevertheless, because of the lack of available data, both in this research, and in the literature, comparisons such as these serve as the only method of extracting information from the far infra-red spectra of complexes IV.

The spectra of $(MeSCH_2CH_2SMeCuCl)_n$ and $(MeSCH_2CH_2SMeCuBr)_n$ are shown in Figures 4.14 and 4.15. The broad peak present in both spectra at 205cm.$^{-1}$ is assigned to terminal Cu-S stretching vibrations. There should, in fact, be two such peaks, but the broadness of the observed peak, even allowing for the inherent broadness of peaks due to M-SMe stretching vibrations, since the SMe group is not an exact point mass, probably indicates that there are two peaks close together. This frequency (205cm.$^{-1}$) is rather low compared with the Cu-S stretching frequencies observed[73] in some cis-1,2dicyanoethylene 1,2dithiolate copper complexes. However, it should be pointed out that the C-S bonds in the latter complexes are covalent rather

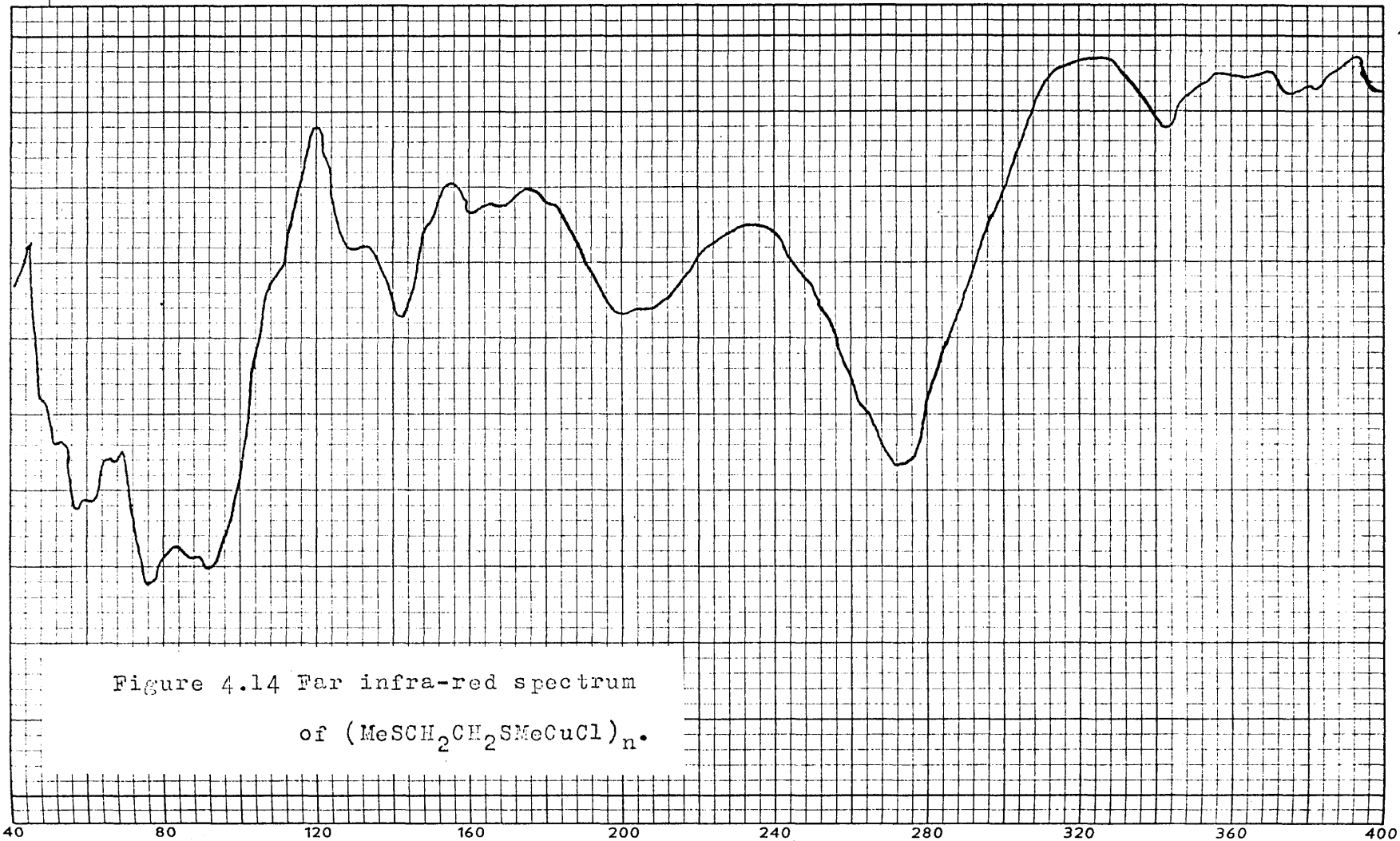


Figure 4.14 Far infra-red spectrum of $(MeSCH_2CH_2SMeCuCl)_n$.

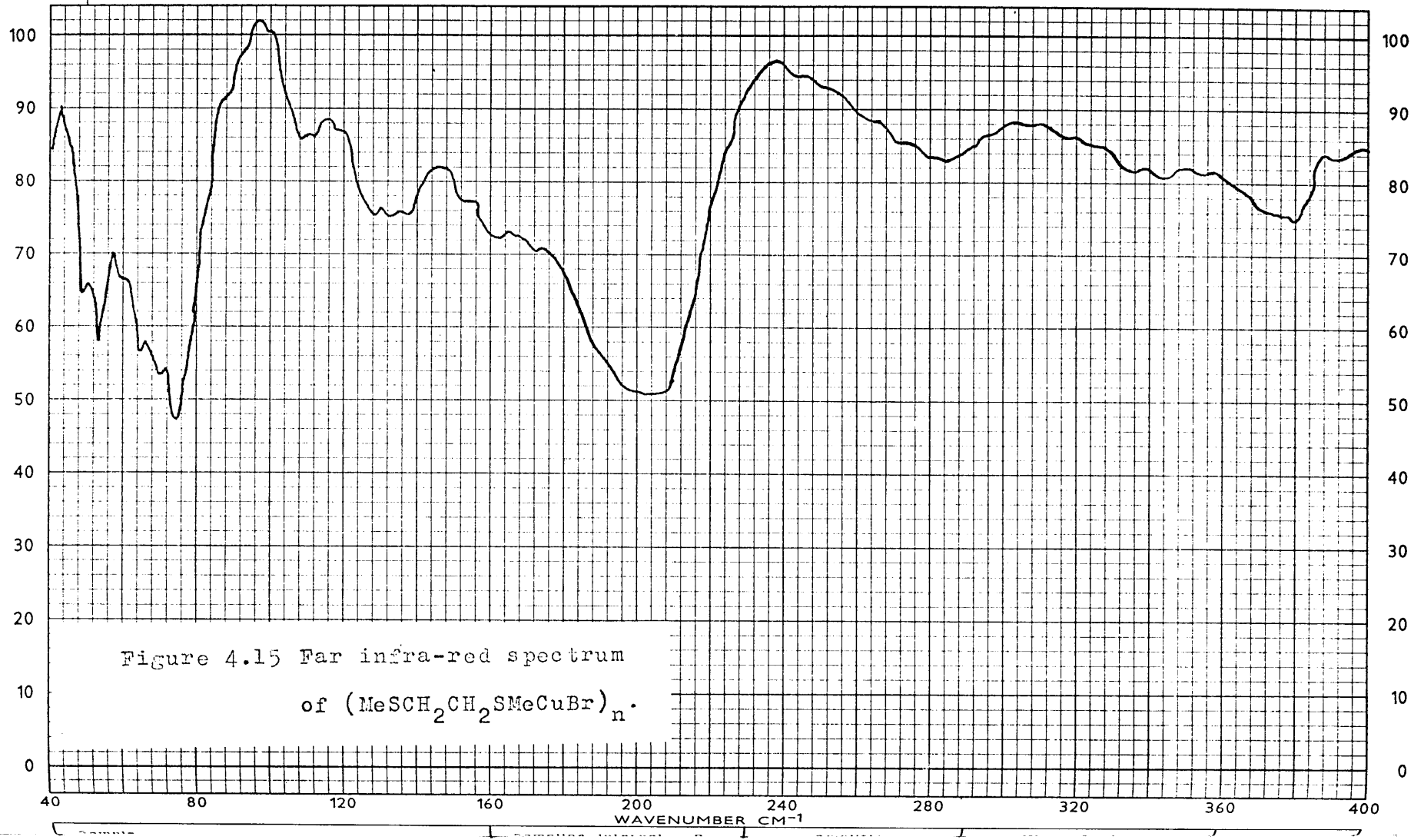


Figure 4.15 Far infra-red spectrum of $(MeSCH_2CH_2SMeCuBr)_n$.

than dative and also the sulphur atoms in the latter complexes are attached to Cu^{II}, so that the two types of Cu-S bonds are not really comparable. It has also been shown[73,100] that M-S stretching frequencies cover a very wide range.

The peak at 272cm.$^{-1}$ in $(MeSCH_2CH_2SMeCuCl)_n$ is thought to arise from a copper-bridging chlorine vibration. This frequency is rather high compared with that observed[101,88] at 228cm.$^{-1}$ in (1,5cyclo-octadiene-CuCl)$_2$. The assignments of Cu-S and Cu-Cl stretching vibrations in $(MeSCH_2CH_2SMeCuCl)_n$ are consistent in themselves in that a weak Cu-S bond would probably be expected with a strong Cu-Cl bond. Also, the copper-bridging chlorine stretching frequency in (1,5cyclo-octadiene-CuCl)$_2$ may be anomalously low because of the high trans-effect of the di-olefin.

In the spectrum of $(MeSCH_2CH_2SMeCuBr)_n$ no peak which can be assigned to a copper-bridging bromine stretching vibration is observed, suggesting that it is masked by the Cu-S stretch at 205cm.$^{-1}$. Support for this suggestion comes from the fact that this peak has gained in intensity on going from $(MeSCH_2CH_2SMeCuCl)_n$ to $(MeSCH_2CH_2SMeCuBr)_n$.

Comparison of the spectrum of $PhSCH_2CH_2SPh$ (Figure 4.5) with that of $(PhSCH_2CH_2SPhCuCl)_n$ (Figure 4.16) (good quality spectra of $(PhSCH_2CH_2SPhCuBr)_n$ were not obtained) suggests

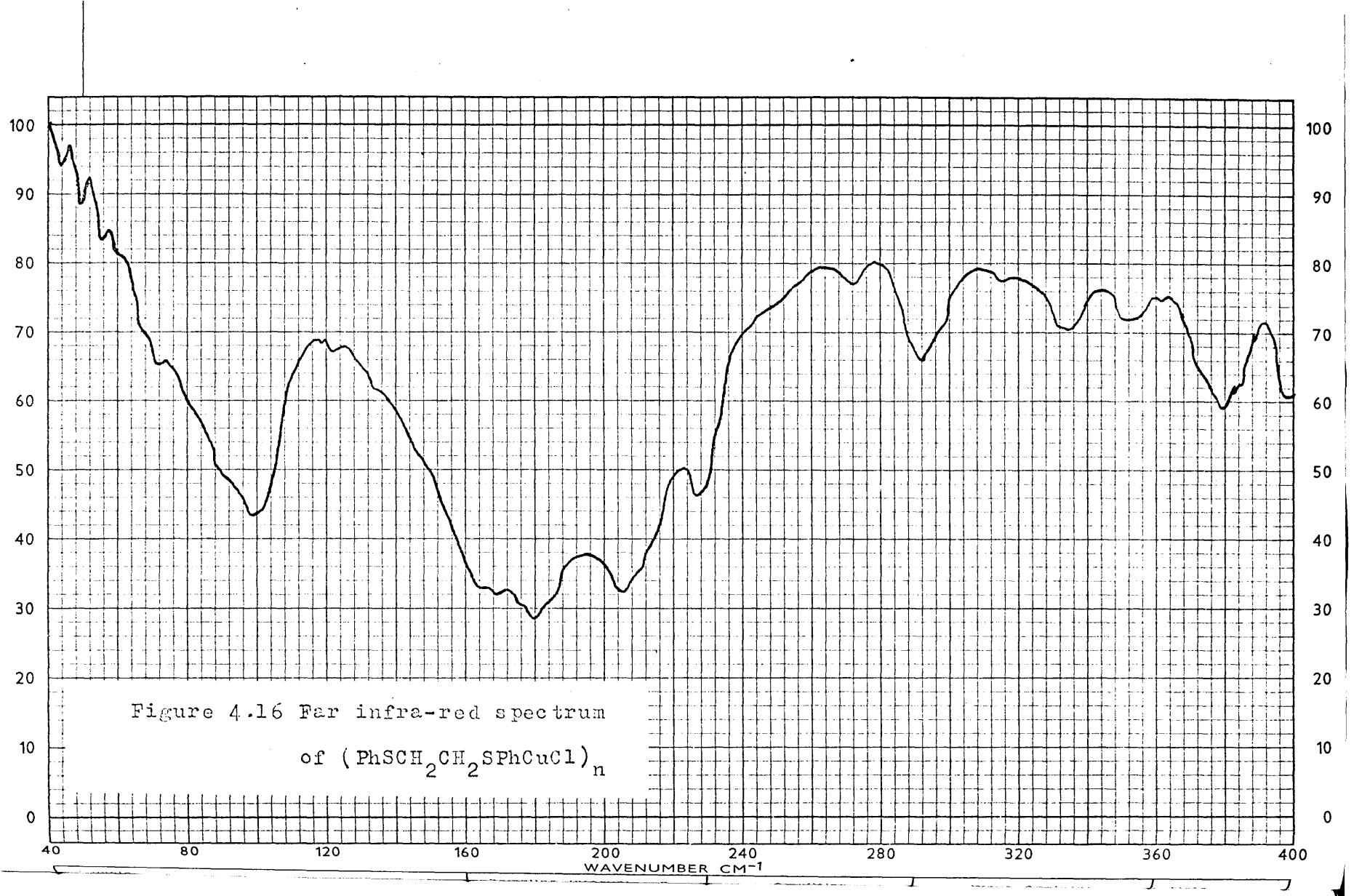


Figure 4.16 Far infra-red spectrum of $(PhSCH_2CH_2SPhCuCl)_n$

that the rather weak peak in the latter at 292cm.$^{-1}$ is due to a copper-bridging chlorine stretching vibration, and that the broad complex of peaks around 180cm.$^{-1}$ may be associated with vibrations of the Cu-SPh moiety. The two peaks at 206 and 228cm.$^{-1}$ in $(PhSCH_2CH_2SPhCuCl)_n$ may arise from similar vibrations to those giving the peaks at 225 and 236cm.$^{-1}$ in the free ligand, altered in position and intensity on complex formation.

All the peaks in the spectra of $(Cp_2Ti[SMe]_2CuX)_2$, V, (X = Cl, Br) (Figures 4.17 and 4.18) below 280cm.$^{-1}$ can be equated with those observed in $Cp_2Ti(SMe)_2$, with the possible exception of the peak at 197cm.$^{-1}$ in $(Cp_2Ti[SMe]_2CuCl)_2$. Thus, no peaks can be assigned to copper-bridging halogen vibrations. The main differences observed when the spectrum of $Cp_2Ti(SMe)_2$ is compared with those of $(Cp_2Ti[SMe]_2CuX)_2$ occur above 280cm.$^{-1}$. No peak is observed in $(Cp_2Ti[SMe]_2CuX)_2$ which corresponds to the peak at 305cm.$^{-1}$ in $Cp_2Ti(SMe)_2$, and instead of the two strong peaks assigned to Ti-S stretching vibrations at 365 and 392cm.$^{-1}$ in $Cp_2Ti(SMe)_2$, weaker peaks at 372 and 378cm.$^{-1}$ in $(Cp_2Ti[SMe]_2CuCl)_2$ and at 372 and 382cm.$^{-1}$ in $(Cp_2Ti[SMe]_2CuBr)_2$ are observed.

The absence of the peak at 305cm.$^{-1}$ in $(Cp_2Ti[SMe]_2CuX)_2$ is difficult to rationalise, but it should be remembered

Figure 4.17 Far infra-red spectrum of $(Cp_2Ti[SMe]_2CuCl)_2$.

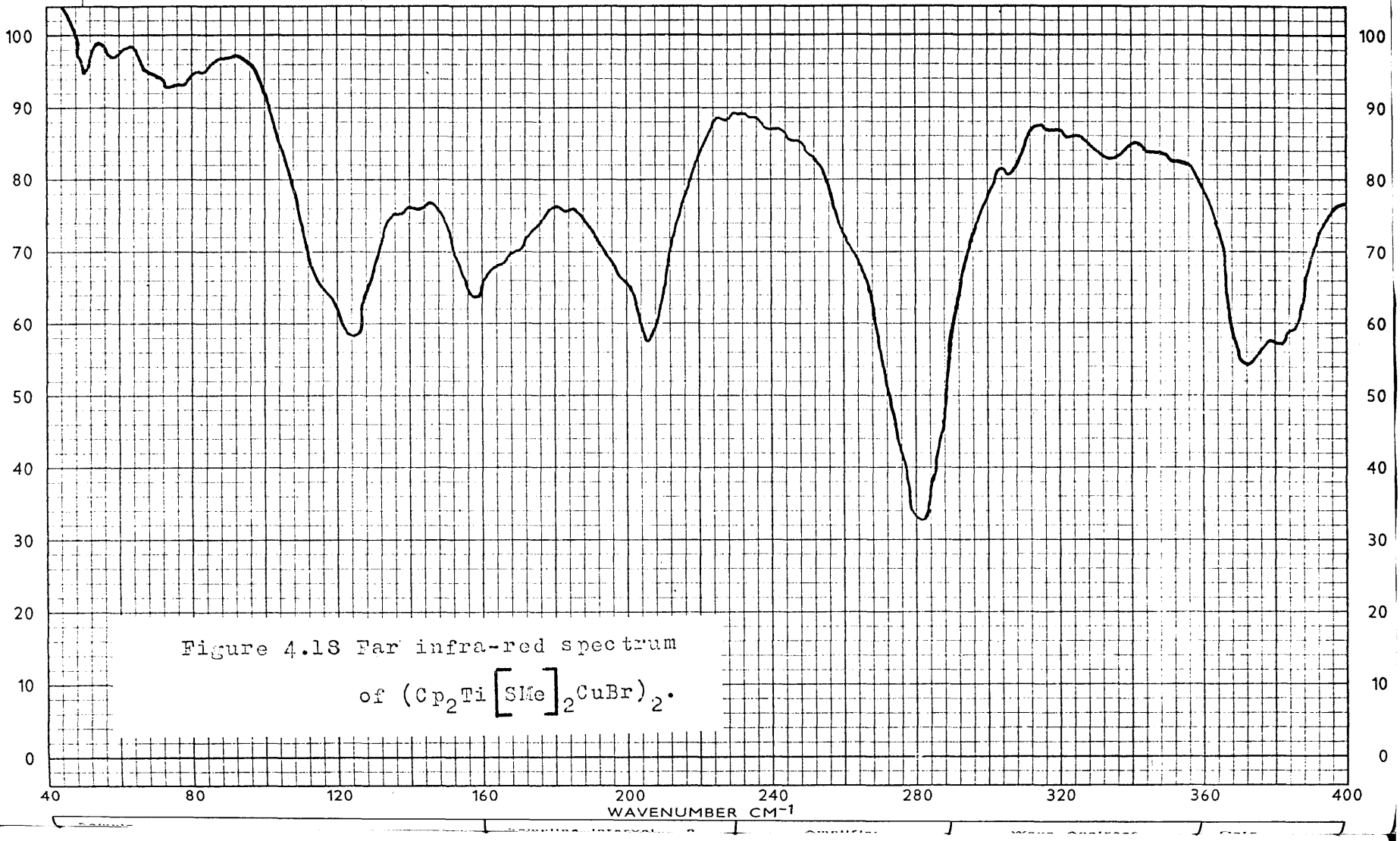


Figure 4.18 Far infra-red spectrum of $(Cp_2Ti[SMe]_2CuBr)_2$.

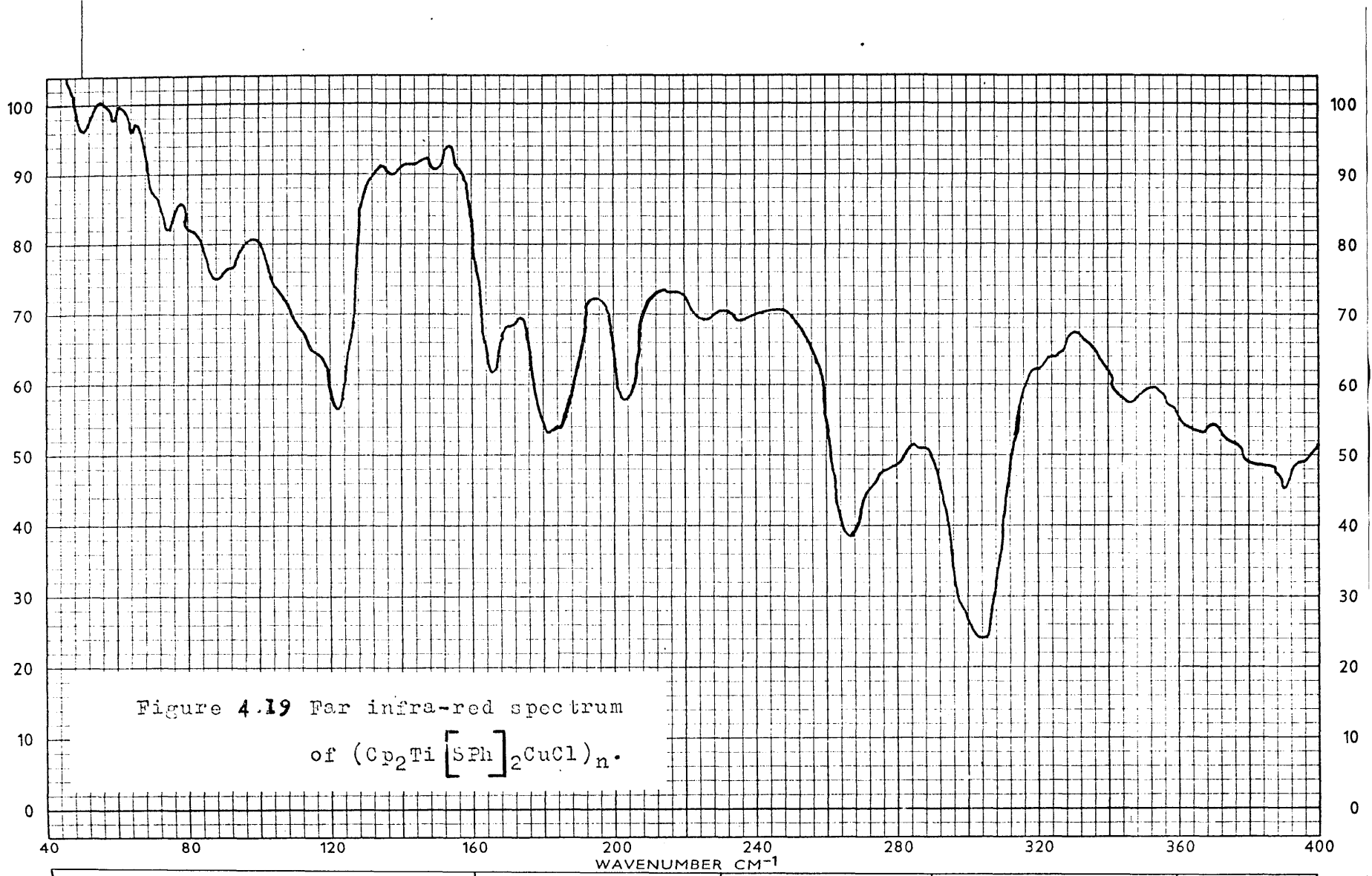


Figure 4.19 Far infra-red spectrum of $(Cp_2Ti[SPh]_2CuCl)_n$.

Figure 4.20 Far infra-red spectrum of $(Cp_2Ti[SPh]_2CuBr)_n$.

that this peak is thought to have moved to lower frequency (296cm.$^{-1}$) in $Cp_2Ti\left[SMe\right]_2W(CO)_4$, and therefore it is reasonable to suppose that the corresponding peak in $(Cp_2Ti\left[SMe\right]_2CuX)_2$ may be masked by the strong peak at 280cm.$^{-1}$.

The peaks between 370 and 382cm.$^{-1}$ in $(Cp_2Ti\left[SMe\right]_2CuX)_2$ are thought to be due to Ti-S stretching vibrations, only slightly modified from those observed in $Cp_2Ti(SMe)_2$. If there had been a drastic modification involving large contributions from the Cu-S stretching vibrations then the peaks arising from simultaneous distortions of the Ti-S and Cu-S bonds would be expected at much lower frequencies since the terminal Cu-S stretching vibrations in $(MeSCH_2CH_2SMeCuX)_2$ are observed at 205cm.$^{-1}$. It is therefore inferred that the Cu-S bond is extremely weak as compared with the Ti-S bond in $(Cp_2Ti\left[SMe\right]_2CuX)_2$.

Comparison of the spectra of $(Cp_2Ti\left[SPh\right]_2CuX)_n$ (Figures 4.19 and 4.20) with those of $(PhSCH_2CH_2SPhCuCl)_n$ and $Cp_2Ti(SPh)_2$ shows much greater diversity than is observed in the methyl complexes. The differences between the spectra of $Cp_2Ti(SPh)_2$, $(Cp_2Ti\left[SPh\right]_2CuCl)_n$, and $(Cp_2Ti\left[SPh\right]_2CuBr)_n$ are most marked above 220cm.$^{-1}$. The peaks at 267 and 304cm.$^{-1}$ in $(Cp_2Ti\left[SPh\right]_2CuCl)_n$ and at 266 and 296cm.$^{-1}$ in $(Cp_2Ti\left[SPh\right]_2CuBr)_n$ can be equated with

the peaks at 264 and 307 cm.$^{-1}$ in $Cp_2Ti(SPh)_2$ although there is considerable dependence on the nature of the halogen as to the relative intensities of these peaks. The strong peaks at 230 and 240cm.$^{-1}$ in $(Cp_2Ti[SPh]_2CuBr)_n$ and the much weaker ones at 224 and 236cm.$^{-1}$ in $(Cp_2Ti[SPh]_2CuCl)_n$ are not observed in $Cp_2Ti(SPh)_2$. Nothing really constructive can be said about the peaks observed between 340 and 400cm.$^{-1}$ in the spectra of complexes IV (R = Ph) since the peaks are too numerous and very weak.

It is, however, suggested that the presence of peaks in the region 220-240cm.$^{-1}$ in complexes IV (R = Ph) which are not observed in $Cp_2Ti(SPh)_2$ may arise from simultaneous distortions of the Ti-SPh and Cu-SPh bonds, but, since this suggestion is of an extremely tentative nature, it would be unwise to comment on the relative Ti-S and Cu-S bond strengths in IV (R = Ph). Alternatively, the apparent changes in spectra between the methyl and phenyl complexes may, yet again, be related to possible steric interactions imposed on the system by the bulky phenyl groups.

As was shown in Chapter 3, all of complexes IV contain a Cu-Ti bond. As the Cu-S bonds in IV (R = Me) appear to be very weak, it is suggested that the Cu-Ti bond is predominant, in IV (R = Me), in holding the two halves of the complexes together, whereas in IV (R = Ph) there may well

be contributions from both the Cu-Ti and Cu-S bonds in holding the complexes together.

4) The complexes $Ph_2PCH_2CH_2PPh_2M[SMe]_2PdCl_2$ (M = Pd, Pt).

The peaks observed in the spectra of the complexes $Ph_2PCH_2CH_2PPh_2M[SMe]_2PdCl_2$, VI, (M = Pd, Pt) are listed in Table 4.1. (Satisfactory spectra, in the range 200-500cm.$^{-1}$, were recorded for the complexes in this, and the following section, using a Grubb Parsons D.M.4 spectrophotometer).

Table 4.1

Complex	Observed Peaks (cm.$^{-1}$)
$Ph_2PCH_2CH_2PPh_2Pd[SMe]_2PdCl_2$	318 306 290(br.) 227(br.)
$Ph_2PCH_2CH_2PPh_2Pt[SMe]_2PdCl_2$	311 292 266(br.)

br. = broad peak.

The two highest energy peaks in the spectra of both complexes are assigned to symmetric and asymmetric Pd-Cl(terminal) stretching vibrations. The other bands are thought to be associated with simultaneous distortions of the M-S (M = Pd, Pt) and Pd-S bonds. In the homodinuclear complex (M = Pd), simultaneous distortions of the Pd-S bonds can still be treated as if the two Pd atoms were not the same, as there are different substituents attached to each.

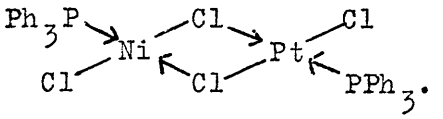
One of the Pd-S stretching frequencies in $MeSCH_2CH_2SMePdCl_2$ has been observed[37] at 228.5cm.$^{-1}$, but in some recently prepared multinuclear complexes with SPh bridging ligands[102], the peaks due to the Pd-S stretching vibrations were not assigned. The spectra of complexes VI suggest that there has been a certain amount of weakening of the M-S covalent bonds (M = Pd, Pt) (compare the Pd-S and Pt-S stretching frequencies in $Ph_2PCH_2CH_2PPh_2M(SMe)_2$ at 307 and 320cm.$^{-1}$ (M = Pd) and 309 and 324cm.$^{-1}$ (M = Pt), (Table 1.1)) and hence fairly strong S→Pd donation is postulated, though it is probably not as strong as that in $MeSCH_2CH_2SMePdCl_2$.

5) The complex $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$.

The complex $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$, VII, was the only member of the series $Ph_2PCH_2CH_2PPh_2M\left[Cl\right]_2PdCl_2$ (M = Ni, Pd, Pt) which was obtained in a characterisable form. (See Chapter 5). This complex shows peaks at 225, 289, 311, and 328cm.$^{-1}$. The two highest energy peaks are assigned to symmetric and asymmetric Pd-Cl(terminal) stretching vibrations. The two at lower energy are thought to be due to Pd-Cl(bridging) stretching vibrations.

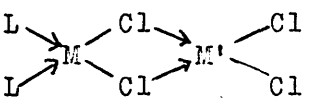
It is interesting to compare the above complex with the complex prepared[103] by the reaction of $(Ph_3P)_2NiCl_2$ with

$(PhCN)_2PtCl_2$. the latter is a white diamagnetic powder which analyses for $(Ph_3P)_2NiCl_2PtCl_2$. The far infra-red spectrum of this complex is very different from that of VII, and is consistent with a structure such as



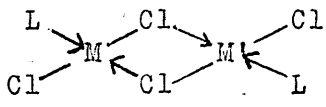
Sharp peaks are observed in the spectrum at 342 and 424cm.$^{-1}$ which can be assigned to terminal Pt-Cl and terminal Ni-Cl stretching vibrations, respectively[37,104]. The assignment of the peak at 424cm.$^{-1}$ as being due to an Ni-Cl vibration is not unambiguous as there are peaks associated with the phosphine (Ph_3P) in this region. The assignment is also based on values[37] for tetrahedrally co-ordinated nickel, and, in order to account for the observed diamagnetism of this complex, it is probable that the nickel atom is in a square planar environment. The other peaks in the spectrum at 226, 247, and 282cm.$^{-1}$ are thought to arise from the simultaneous distortions of the Ni-Cl and Pt-Cl bonds in the NiClPtCl ring.

The probable structure of the Ni/Pt complex suggests that if <u>cis</u> complexes of the form



are present in a reaction mixture, they may well isomerise

to the more stable trans form



In complexes VI (4, above) and VII in which $L_2 = Ph_2PCH_2CH_2PPh_2$ the two ends of the ligand are, for steric reasons, bound to the same metal atom and cannot isomerise in the above manner, and must, therefore, remain in the less stable cis form.

CHAPTER 5

Attempted Preparations of Other Multi-Heteronuclear Complexes.

In this chapter attempts will be made to rationalise the results of reactions which, although designed to produce multi-heteronuclear complexes, yielded what can best be described as products resulting from rearrangements and/or decompositions of the starting materials and/or reaction intermediates.

These reactions can be divided into 3 groups:-

a) Reactions of $Cp_2Ti(SR)_2$ with transition metal carbonyls, transition metal carbonyl halides, and other transition metal halides.

b) Reactions of silanes with one or more transition metal residues.

c) Reactions of cobalt carbonyl derivatives with titanium complexes.

Reactions (a) were designed to prepare complexes containing titanium and another transition metal linked together by organothio bridges, as already described in Chapters 2 and 3. Reactions (b) were intended to produce complexes containing 2 of the same or 2 different transition metals linked by $>SiR_2$ bridges. Using reactions (c) it was hoped to produce hetero-di and -trinuclear complexes containing Co-Ti or Co-Ti-Co skeletons respectively, in which the 2(3) metal atoms are joined together by Co-Ti σ-bonds.

It is easy to say that the desired products were not obtained because the starting materials or reaction intermediates are labile with respect to rearrangement or decomposition, but it is necessary to go a bit deeper than this, and to postulate reasons why these reactions failed to produce the desired products whereas similar reactions have yielded stable complexes as described in the literature, or already discussed in this work.

1) Reactions of $Cp_2Ti(SR)_2$ (R=Me, Ph).

The experimental evidence suggests that in the reactions of $Cp_2Ti(SR)_2$ with $Mn(CO)_5Br$, $Ru(CO)_3Cl_2$ T.H.F., and $RuCl_3/CO/MeOCH_2CH_2OMe$ solution there is transfer of one or more halogen atoms from the metal carbonyl halide to

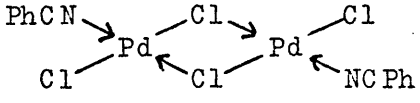
titanium and transfer of one or more organothio groups from $Cp_2Ti(SR)_2$ to the other transition metal. The result of such rearrangements in the above reactions is to give the observed products $(Mn(CO)_3SR)_4$ and $(Ru(CO)_3SR)_n$ together with $Cp_2Ti(SR)Br$ and Cp_2TiCl_2, respectively. ($Cp_2Ti(SR)Br$ was not observed as such, but its presence can be inferred (Experimental 7c)). Reactions of this type have been observed when thiosilanes[105] and thiostannanes[106] are reacted with transition metal halides, especially $Mn(CO)_5Br$, giving halosilanes or halostannanes together with the corresponding transition metal organothio complex.

Compared with other transition metals, titanium^{IV} seems to have a much stronger affinity for halogens than for sulphur as it has been found[107] that the reaction of Cp_2TiCl_2 with $AgSCF_3$ gives Cp_2TiF_2 whereas $CpCr(NO)_2Cl$ with $AgSCF_3$ gives $CpCr(NO)_2SCF_3$. The transition metal carbonyls to the right of Group VI all seem to have a strong affinity for sulphur judging by the number of sulphur containing complexes of these metals that are known[108].

The formation of the observed products from the reactions noted above, can therefore be rationalised on the basis of the great affinity Ti^{IV} has for halogens, and probably, though to a lesser extent, the affinity of the other transition metal for sulphur.

Similar reasoning can be used to explain why the reaction of $Cp_2Ti(SMe)_2$ with $(PhCN)_2PdCl_2$ gives $\left[Pd(SMe)_2\right]_n$ and Cp_2TiCl_2. The complex $Cp_2Ti\left[SPh\right]_2PdCl_2$ has, however, been claimed[103], which suggests that -SPh groups attached to titanium are not as labile as the corresponding -SMe groups.

Having mentioned reactions involving $(PhCN)_2PdCl_2$, it is interesting to note that although the complex $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$, VII, (Chapter 4) was obtained from the reaction of $Ph_2PCH_2CH_2PPh_2PdCl_2$ and $(PhCN)_2PdCl_2$, the other members of the series $Ph_2PCH_2CH_2PPh_2M\left[Cl\right]_2PdCl_2$ (M = Ni, Pt) were not obtained from the corresponding reactions. The absence of $(PhCN)_2PdCl_2$ from the observed products ($PdCl_2$ and $Ph_2PCH_2CH_2PPh_2MCl_2$) suggests that the desired products may have a transient existence in solution. If there had simply been no reaction, $(PhCN)_2PdCl_2$ would have been expected in the products. However, $(PhCN)_2PdCl_2$ has been shown to have a <u>trans</u> structure in the solid[109,110], and substitution reactions are thought to go via the dinuclear species[111]



so that unless the incoming substituent is a good σ-donor, this dinuclear intermediate may decompose to $PdCl_2$ and liberate PhCN on work up. As the halogen atoms in

$Ph_2PCH_2CH_2PPh_2MCl_2$ (M = Ni, Pt) are probably poor σ-donors, the absence of $(PhCN)_2PdCl_2$ from the observed products may result from decomposition of the postulated dinuclear intermediate. On the other hand, the chlorine atoms in $Ph_2PCH_2CH_2PPh_2PdCl_2$ and the sulphur atoms in $Ph_2PCH_2CH_2PPh_2M(SMe)_2$ (M = Pd, Pt) would seem to be strong enough σ-donors to allow formation of the complexes $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$ and $Ph_2PCH_2CH_2PPh_2M\left[SMe\right]_2PdCl_2$.

Returning to ligand replacement reactions involving $Cp_2Ti(SR)_2$, the great ease of formation of $\left[CpFe(CO)_2\right]_2$ from iron carbonyls in the presence of a source of cyclopentadienyl rings, can be invoked to explain its formation in the reaction of $Cp_2Ti(SPh)_2$ with maleic anhydride-$Fe(CO)_4$. The work required to pull a cyclopentadienyl ring away from titanium, especially one which is attached by strong covalent bonds, must be considerable, and illustrates the great stability of $\left[CpFe(CO)_2\right]_2$.

2) Reactions of substituted silanes with transition metal carbonyl residues.

Over the last few years, many complexes containing silicon bonded to a transition metal have been prepared.

Two main routes have been used:-

a) The elimination of hydrogen, by the method of Chalk and Harrod[112] (See Introduction, 2a, p.2).

b) Nucleophilic displacement of a halogen from a halosilane (See Introduction, 1a, p.2).

In the vast majority of complexes, each silicon atom is bonded to only one transition metal as, for example, in $Me_3SiMn(CO)_5$[113] and $Fe(CO)_4(SiCl_3)_2$[7]. Very few complexes are known in which the silicon atom forms a bridge between two or more transition metals, as in the recently reported[114] $(OC)_4Co[SiH_2]Co(CO)_4$, and the unusual complex $CH_2{=}CHSi(Co(CO)_4)_3$[115] in which the silicon atom forms a bridge between 3 cobalt atoms. Complexes containing other Group IV elements, notably Ge and Sn, in which the Group IV element forms a bridge between two transition metals are well known, e.g. $I_2Ge(Co(CO)_4)_2$[116], $Ph_2Sn(Re(CO)_5)_2$[117], and $(OC)_5Mn[SnPh_2]WCp(CO)_3$[4].

The differing properties of Si on the one hand, and Ge and Sn on the other, in this respect, have proved impossible to rationalise completely, but in some cases, may simply arise from the lability or the inactivity of the reaction intermediates in the silicon series.

The main reactions which were carried out are listed

in a-d, below, together with the desired products from these reactions. (See Experimental, Section 10, for complete details of these reactions).

a) $2NaCo(CO)_4 + Cl_2SiMe_2 \longrightarrow Me_2Si(Co(CO)_4)_2 + 2NaCl.$

b) $Co_2(CO)_8 + H_2SiMePh \longrightarrow MePhSi(Co(CO)_2)_2 + H_2.$
(or $2HCo(CO)_4 \longrightarrow 2H_2$).

c) $(OC)_4CoSiMe_2Cl + Na^+M^- \longrightarrow (OC)_4CoSiMe_2M + NaCl.$
(M^- is a metal carbonyl anion).

d) $2CpFe(CO)_2SiMe_2H + Co_2(CO)_8 \longrightarrow 2CpFe(CO)_2Si(Me_2)Co(CO)_4 + H_2.$

There is no conclusive evidence that any of the desired complexes were present in the mixtures of products obtained from reactions a-d, and certainly none of the desired complexes were obtained in a pure form.

Most of the reactions were carried out at 0°C and above, and this may constitute one of the major reasons why the desired products were not obtained, as $H_2Si(Co(CO)_4)_2$ has subsequently been obtained[114] by the reaction of $NaCo(CO)_4$ and H_2SiI_2 at -50°C in dimethyl ether.

When reaction (a) was carried out in T.H.F. or diethyl ether at room temperature, the intermediate complex,

$Me_2SiClCo(CO)_4$, decomposed rapidly to $CoCl_2$. That this was, indeed, the complex undergoing decomposition was inferred from the fact that pure $Me_2SiClCo(CO)_4$, prepared by the reaction of $Co_2(CO)_8$ and Me_2SiHCl, decomposed in the same manner. Chlorosilanes are, in general, reactive towards T.H.F., usually giving products resulting from ring opening of the cyclic ether[118]. Thus, unless reaction (a) is carried out in a more inert solvent or at lower temperatures, it is not applicable to the preparation of the desired complexes.

The complex $MeH_2SiCo(CO)_3$[119] has been prepared by the reaction of $Co_2(CO)_8$ and H_3SiMe. This suggests that the replacement of the first hydrogen is easier than the replacement of the others, so that the $Co_4(CO)_{12}$ observed in reaction (b) may simply be a decomposition product of the probable intermediate $Me_2HSiCo(CO)_4$, as the complexes $MeH_2SiCo(CO)_4$[119a] and $H_3SiCo(CO)_4$[114] readily undergo cleavage of the Si-Co bond.

The complex $Me_2SiClCo(CO)_4$, used in reaction (c), is less easily hydrolysed than simple chlorosilanes suggesting that it is less susceptible to nucleophilic attack. This seems to be the case since no reaction was observed between $Me_2SiClCo(CO)_4$ and $NaCo(CO)_4$ in toluene, other than decomposition to $Co_4(CO)_{12}$ at high temperatures. Only

with the much more nucleophilic[120] $[CpFe(CO)_2]^-$ was a reaction observed at room temperature, but the mixture of products from this reaction could not be separated.

The complex $CpFe(CO)_2SiMe_2H$ prepared by the reaction of $NaCpFe(CO)_2$ with Me_2SiHCl was found to decompose at room temperature, giving $[CpFe(CO)_2]_2$ (a recently announced preparation[121] indicates rather greater stability) indicating a rather weak Fe-Si bond. Thus, when $Co_2(CO)_8$ is reacted with $CpFe(CO)_2SiMe_2H$ (reaction d) there may be cleavage of the Fe-Si bond rather than the Si-H bond leading to the formation of $CpFe(CO)[CO]_2Co(CO)_3$[16] and possibly $Me_2HSiCo(CO)_4$ which probably decomposes, as postulated in reaction (b), to $Co_4(CO)_{12}$.

These observations suggest that the failure to prepare complexes containing an M-Si-M' skeleton may be due to the chemical properties of the intermediates, $M\text{-}SiR_2Cl$ and $M\text{-}SiR_2H$ (M and M' are transition metal carbonyl residues). In $M\text{-}SiR_2Cl$ the silicon seems to be deactivated towards nucleophilic attack whereas $M\text{-}SiR_2H$ seems to be thermally unstable.

The reason(s) why the intermediates in the germanium and tin series of reactions give the desired complexes whereas those in the silicon series do not remains unexplained, but may be related to the relative amounts of

π-bonding between the Group IV metal and the transition metal. Although this is an area of intensive research at present[122], there is not yet sufficient data to attempt an explanation of the differences between the silicon and the germanium and tin series of reactions.

3) Reactions of titanium complexes with cobalt carbonyl derivatives.

Because of the fairly close analogy that runs through the chemistry of titanium and the chemistry of tin, and because complexes containing titanium covalently bonded to other transition metals are known[123], reactions were studied in which titanium might react in a similar manner to tin, giving complexes containing Ti-Co bonds.

The reactions carried out, together with the desired products are listed in a-d, below. (For complete details of the reactions, see Experimental, Section 11).

a) $Cp_2TiCl_2 + 2NaCo(CO)_4 \longrightarrow Cp_2Ti(Co(CO)_4)_2 + 2NaCl.$

b) $\left[Cp_2Ti^{III}Cl\right]_2 + 2NaCo(CO)_4 \longrightarrow 2Cp_2Ti^{III}Co(CO)_4 + 2NaCl.$

c) $\left[\begin{matrix}Cp_2Ti\text{-}O\text{-} \\ \quad\quad Cl\end{matrix}\right]_2 + 2NaCo(CO)_4 \longrightarrow \left[\begin{matrix}Cp_2Ti\text{-}O \\ \quad\quad Co(CO)_4\end{matrix}\right]_2 + 2NaCl.$

d) $Cp_2TiMe_2 + 2HCo(CO)_4 \longrightarrow Cp_2Ti(Co(CO)_4)_2 + 2CH_4.$

In each of the above reactions, the only product which could be characterised was $CpCo(CO)_2$. As $CpCo(CO)_2$ only appeared when all the T.H.F. (solvent) was removed it was thought that the T.H.F. might have some stabilising influence on the complex formed initially. When the reactions were carried out in the presence of triphenyl phosphine only $Ph_3PCo(CO)_3Co(CO)_3PPh_3$[124] was obtained. In these reactions, a-d, it is suggested that something approaching the expected reaction takes place, but the complex formed is unstable, and breaks down to give the much more stable $CpCo(CO)_2$.

CONCLUSIONS

From the observed results, the ligand replacement reaction, in which loosely bound ligands on a transition metal are replaced by a "transition metal containing ligand", is the most productive route to multi-heteronuclear complexes. (Chapters 2 and 3). Nucleophilic displacement and elimination reactions are found (Chapter 5) to suffer from the disadvantage that the actual preparation of the heteronuclear species is a 2 step process, and the products from the first step tend to be either too stable or too unstable for the second step to take place. Both of these types of reaction have been used extensively elsewhere (See Introduction) to prepare heteronuclear complexes, and therefore the above remarks are confined to those reactions whereby attempts were made to prepare complexes containing silicon or titanium bonded to transition metals.

The ligand replacement reaction is limited to a certain extent in that the potential bridging atom in the "transition metal containing ligand" must have at least one

lone pair suitable for donation to another transition metal. Also, some of the ligand replacement reactions lead to complexes which rearrange to give more stable homonuclear complexes, illustrating that the method of preparation is always limited by the stability of the desired complex.

The heteronuclear complexes which were prepared fall into two groups:-

a) Those which contain a metal-metal bond.

b) Those which do not contain a metal-metal bond.

The complexes $Cp_2Ti\left[SR\right]_2M'(CO)_4$, I, (R = Me, Ph; M' = Cr, Mo, W) (Chapter 2), and $(Cp_2Ti\left[SR\right]_2CuX)_n$, IV, (R = Me, Ph; X = Cl, Br) (Chapter 3) are members of group (a), whereas $(L\text{-}L)M\left[SR\right]_2M'(CO)_4$, II, (L-L = 1,2 bis-diphenylphosphino ethane, o-phenylene bis-diethylarsine; M = Pd, Pt; R = Me, Ph; M' = Cr, Mo, W) (Chapter 2), $Ph_2PCH_2CH_2PPh_2M\left[SMe\right]_2PdCl_2$, VI, (M = Pd, Pt) (Chapter 4), and $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$, VII, (Chapter 4), come into group (b).

The metal-metal bond in complexes I and IV is not necessary to explain their observed diamagnetism as they would still be diamagnetic if no metal-metal bond were present. The metal-metal bonds are of a dative nature and can be looked upon as the donation of an electron pair from M' or Cu to Ti in I and IV, respectively.

The closeness of approach of the two metal atoms and hence the strength of the metal-metal bond appears to be restricted by steric interactions between the cyclopentadienyl rings on titanium. There may also be a further limitation on the metal-metal bond strength in I and IV (R = Ph) because of steric interactions between the cyclopentadienyl and phenyl rings.

From far infra-red evidence, it is tentatively suggested that the S→M' bond in I (R = Me) is strong and that the S→Cu bond in IV is weak. There is also evidence that the Cu-Ti bond in IV (R = Me) may be more instrumental in holding the two halves of the complex together than is the Cu-Ti bond in IV (R = Ph).

There appears to be evidence for structural differences between members of I and IV. Complexes I are thought to exist in two isomeric forms with one isomer predominating when R = Me, and the other predominating when R = Ph. Complexes IV are thought to exist as oligomers, and the number of monomer units, $Cp_2Ti\left[SR\right]_2CuX$, present, may well depend on the nature of R.

The complexes of group (b) are stable as solids, but they tend to decompose rapidly in solution. It may well be that it is the inherent stability of the solids, due to

lattice effects, that leads to the formation of the complexes.

These complexes, which do not have a metal-metal bond, must be held together by donation of one of the lone pairs on sulphur or chlorine (sulphur in complexes II and VI, chlorine in VII) to the other metal in the complex. There is, in addition, in complexes II, however, a theoretical possibility of an unsupported π-bond between the two metals, formed by donation of an electron pair from M' to M, but no evidence for the existence of such a bond has been found.

It seems probable, although there is no proof, that all the complexes of group (b) are of similar structure, having a planar MBM'B ring with acute BMB angles and obtuse MBM' angles because of the repulsive forces between M and M'. This structure would be in direct contrast to the acute TiSMo angles and obtuse STiS and SMoS angles observed in the molecular structure of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$ [62] which has an Mo→Ti bond.

Complexes I and IV are probably best looked upon as true heteronuclear, or small cluster complexes where the two metals cannot be regarded separately since the properties of one metal are dependent on, and are reflected

in, the characteristics of the other. The complexes II, VI, and VII which do not contain metal-metal bonds are best looked upon as complexes of Group VI metals (complexes II) or palladium (complexes VI and VII) in which two of the co-ordination sites are occupied by a ligand which contains another transition metal. In this respect, they are similar to complexes such as $Me_2Sn\left[PPh_2\right]_2Ni(CO)_2$[9].

As was hoped (See Introduction) it has proved possible to obtain information about interactions between two metals using spectroscopic methods to compare one side of the complex with the other. Although this information is far from conclusive for many of the complexes prepared, since their properties do not lend themselves to the full range of spectroscopic techniques, the postulates made concerning complexes I have been confirmed by the molecular structure of $Cp_2Ti\left[SMe\right]_2Mo(CO)_4$[62].

EXPERIMENTAL

Section 1.

General.

Instrumentation.

Infra-red spectra (4000-400cm.$^{-1}$) were run on Perkin-Elmer Grating Spectrophotometers, models 225, 457, and 257. Carbon monoxide and the 1603cm.$^{-1}$ band in polystyrene were used for calibration. The electronic spectra (10,000-40,000cm.$^{-1}$) of both solids and solutions were recorded using a Beckman DK-2A spectrophotometer with a lead sulphide cell as detector at wavenumbers less than 14,000cm.$^{-1}$ and a photomultiplier tube at higher frequencies. The far infra-red spectra (400-40cm.$^{-1}$) were obtained using an RIIC FS 720 interferometer coupled with an F.T.C.100 analog to digital computer. The resolution of this instrument is ±5cm.$^{-1}$ and the frequency is checked using an electronic pulse at 156cm.$^{-1}$. Preliminary ^{1}Hn.m.r. spectra were run at 60M.Hz. on a Varian R10 instrument. More detailed spectra were obtained at 220MHz. on a

Varian HR-220 spectrometer. Both instruments were fitted with cold temperature probes. Magnetic susceptibility measurements were carried out using a Guay balance.

Microanalyses.

Microanalyses were carried out by C.E. O'Brien and his colleagues at Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, Runcorn.

Reaction Conditions.

Reactions were carried out under nitrogen or in vacuo, where appropriate. The solvents used, mainly tetrahydrofuran (T.H.F.) and toluene, were dried (See below) and purged with nitrogen before use. Reaction vessels were pumped out and opened to nitrogen 3 times before introduction of the solvent and reactants. The solvents which were used under vacuum conditions were degassed after purging with nitrogen.

Solvents.

Toluene, with low sulphur content, was dried by standing it over sodium wire. T.H.F. was distilled directly into the reaction flask after it had been dried with NaOH pellets

and sodium wire, and the characteristic blue colour had been obtained on addition of further sodium wire and benzophenone. Methylene chloride was dried by running it down an activated alumina column. All other solvents used were "AnalaR" and no special drying techniques were employed.

The progress of certain reactions was followed by changes in the infra-red spectrum of the reaction mixture. This technique was used most extensively in reactions involving metal carbonyls.

Starting materials, unless otherwise stated, were prepared by the method given in the attached reference.

Section 2.

Preparation of Some Dichloride Complexes of Palladium^{II} and Platinum^{II}.

The complexes have the general formula $(L\text{-}L)MCl_2$, where L-L = 1,2 bis-diphenylphosphino ethane, 1,2 bis-dimethylphosphino ethane, bis-diphenylphosphino methane, O-phenylene bis-diethylarsine, 1,5 dithiahexane, 1,2 dithiophenyl ethane; M = Pd, Pt.

a) Preparation of Chelating Ligands.

1,5 dithiahexane was obtained commercially, O-phenylene bis-diethylarsine was a gift from Mr.B. Dobbs, Imperial Chemical Industries Limited, 1,2 bis-diphenylphosphino ethane[125], bis-diphenylphosphino methane[125], and 1,2 dithiophenyl ethane[126] were prepared according to the literature.

Preparation of 1,2 bis-dimethylphosphino ethane, $Me_2PCH_2CH_2PMe_2$.

60gms. (0.31 moles) of $Me_2P(S)P(S)Me_2$[127] were heated

with 100gms. of iron powder in a vacuum distillation apparatus until all the $Me_2P(S)P(S)Me_2$ had melted (250°C). On heating more strongly (with a Bunsen burner), tetramethyl diphosphine, Me_2PPMe_2, distilled off. Me_2PPMe_2 (24gms., 0.2moles) was cleaved by stirring for 12 hours with Li (3gms.) in 200mls. T.H.F. containing a catalytic amount of naphthalene. 9.9gms. (0.1mole) of 1,2 dichloroethane, in 30mls. T.H.F., were added dropwise to the solution of $LiPMe_2$, the reaction mixture being kept at -40°C. When addition was complete, the solution was stirred at room temperature for a further 2 hours. Distillation of the crude reaction mixture yielded the desired product (B.Pt. 50-65°C, 10mm.Hg). The product (18.8gms.; 31% based on $Me_2P(S)P(S)Me_2$) was sealed in ampoules and used without further purification.

b) Preparation of $(L\text{-}L)MCl_2$.

Complexes of the type $(L\text{-}L)MCl_2$ are normally prepared by the reaction of a solution containing the chelating ligand with an aqueous solution of Na_2MCl_4 or K_2MCl_4 (M= Pd, Pt) and subsequent decomposition, by HCl or dimethylformamide, of the intermediate salt formed[35,128]. A better method of preparing these complexes was to treat a toluene solution of $(PhCN)_2MCl_2$[129] (M = Pd, Pt) with an

equimolar amount of the chelating ligand. After initial preparations by the former reaction, the latter was used exclusively.

Preparation of $Ph_2PCH_2CH_2PPh_2PdCl_2$.

2,0gms. (0.05moles) of $Ph_2PCH_2CH_2PPh_2$ were dissolved in 100mls. of toluene, and added to a solution of 1.9gms. (0.05moles) of $(PhCN)_2PdCl_2$ in 50mls. of toluene. The reaction mixture was stirred at 70°C for 2 hours and a white precipitate separated out. The solid was removed by filtration, washed several times with toluene, and crystallised from hot dimethylformamide. (Yield = 2.5gms., 80%). The product was found, from its analysis and melting point, to be identical with a sample prepared by the reaction of $Ph_2PCH_2CH_2PPh_2$ with Na_2PdCl_4[35].

The following complexes were prepared in a similar manner:- $Ph_2PCH_2CH_2PPh_2PtCl_2$[35], $Me_2PCH_2CH_2PMe_2PdCl_2$[128], $Me_2PCH_2CH_2PMe_2PtCl_2$[128], $MeSCH_2CH_2SMePdCl_2$[130], $PhSCH_2CH_2SPhPdCl_2$[131], $Ph_2PCH_2PPh_2PdCl_2$, $C_6H_4(AsEt_2)_2PdCl_2$, and $C_6H_4(AsEt_2)_2PtCl_2$. The last 3 of these complexes have not been reported previously.

$Ph_2PCH_2PPh_2PdCl_2$, white needles; does not melt below 300°C; (Found: C,53.1; H,3.9. $C_{25}H_{22}Cl_2P_2Pd$ requires: C,53.5; H,4.0%).

The diarsine complexes were characterised by their far

infra-red spectra, but not by analysis. However, their mercaptide derivatives were fully characterised (Section 3a).

1,5 hexadiene-$PtCl_2$ was prepared by the reaction[132] of 1,5 hexadiene with an aqueous solution of K_2PtCl_4.

Section 3.

Preparation of Transition Metal Mercaptide Complexes.

a) Mercaptide complexes of Pd^{II} and Pt^{II}.

The complexes have the general formula $(L\text{-}L)M(SR)_2$ (L-L = 1,2 bis-diphenylphosphino ethane, Ophenylene bis-diethyl arsine; M = Pd, Pt; R = Me, Ph).

Complexes of the type $L_2M(SR)_2$ (L = tri-alkyl/-aryl phosphines; M = Ni, Pd: R = Et, Ph) have been prepared [133] by treating L_2MCl_2 with an ethanolic solution of NaSR (R = Et, Ph).

Sodium methyl mercaptide, NaSMe, and sodium phenyl mercaptide were prepared by the reaction of sodium shot with the corresponding thiol. (Low temperature proceedures, similar to those required for the preparation of $(L\text{-}L)M(SMe)_2$ as described below, were necessary for the preparation of NaSMe). The white solids were filtered off from the solvent (diethyl ether), washed with ether, and stored under nitrogen until required. NaSMe was also prepared by cleaving dimethyl disulphide, MeS-SMe, with Na/ liquid ammonia, and washing the product with liquid ammonia at -50°C.

The yields of the palladium and platinum mercaptide complexes, $(L\text{-}L)M(SR)_2$, obtained by the literature method[133] for the preparation of the palladium complexes, were low due to the concurrent formation of an uncharacterised water soluble complex. A better method of preparation of $(L\text{-}L)M(SR)_2$, was to react a large excess of the thiol (MeSH or PhSH) with $(L\text{-}L)MCl_2$ in the presence of triethylamine, NEt_3. Although both methods were used, the latter was used much more extensively.

Preparation of $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$.

A suspension of 2.0gms. (3.5m.moles) of $Ph_2PCH_2CH_2PPh_2PdCl_2$ in 150mls. of toluene, in a 250ml. flask fitted with a dry-ice condensor, was cooled to -78°C in a bath of solid CO_2/acetone. 1.4mls. (1gm.; 10m.moles) of triethylamine and 1ml. (0.8gms.; 17m.moles) of methane-thiol were added and the reaction mixture was allowed to heat up to room temperature with the dry-ice condensor still in position. The suspension was stirred for 8 hours, and the colour changed from white to yellow. The dry-ice condensor was then removed and excess MeSH (B.Pt. 6°C) was allowed to evaporate off. The reaction mixture was filtered, the residue was washed with water, then cold ethanol, and crystallised from hot ethanol as yellow crystals.

$Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$, M.Pt. 193-7°C; (Found: C,56.4: H,5.1; P,10.2; S,10.2. $C_{28}H_{30}P_2PdS_2$ requires: C,56.2; H,5.2; P,10.3; S,10.6%).

In the analogous preparations where thiophenol was used instead of methane-thiol, there was no need for initial cooling or for the use of a dry-ice condensor, otherwise the reaction conditions and purification of the products were the same.

Similarly prepared were:-

$Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$, yellow crystals; M.Pt. 240-2°C; (Found: C,48.9; H,4.4; P,8.6; S,9.1. $C_{28}H_{30}P_2PtS_2$ requires: C,48.9; H,4.4; P,9.0; S,9.3%).

$Ph_2PCH_2CH_2PPh_2Pt(SPh)_2$, yellow rods; M.Pt. 222-5°C; (Found: C,56.4; H,4.2. $C_{38}H_{24}P_2PtS_2$ requires: C,56.2; H,4.2%).

$C_6H_4(AsEt_2)_2Pd(SMe)_2$, (recrystallised from toluene); orange crystals; M.Pt. 151-3°C; (Found: C,35.4; H,5.8. $C_{16}H_{30}As_2PdS_2$ requires: C,35.2; H,5.6%).

$C_6H_4(AsEt_2)_2Pt(SMe)_2$, (recrystallised from toluene); pale yellow crystals; M.Pt. 150-2°C; (Found: C,31.0; H,4.7. $C_{16}H_{30}As_2PtS_2$ requires: C,31.0; H,4.7%).

$\underline{C_6H_4(AsEt_2)_2Pd(SPh)_2}$, (recrystallised from toluene); red/orange crystals; M.Pt. 165-8°C; (Found: C,46.9; H,5.3. $C_{28}H_{36}As_2PdS_2$ requires: C,47.0; H,5.1%).

The above, air stable complexes were obtained in yields of over 80%. A sample of $Ph_2PCH_2CH_2PPh_2Pd(SPh)_2$ prepared by the above route had the same melting point and infra-red spectrum as that obtained by the literature[133] proceedure.

Attempts to prepare $Me_2PCH_2CH_2PMe_2M(SR)_2$ were unsuccessful in that the reactions gave 100% yields of a yellow/orange water soluble species of unknown identity.

The reaction of $PhSCH_2CH_2SPhPdCl$ with MeSH and NEt_3 under the above conditions liberated $PhSCH_2CH_2SPh$, and yielded a solid which was extremely insoluble in all solvents tried. The analytical figures for this solid, although showing a rather wide variation over several reactions, approximate to those required for $\left[Pd(SMe)_2\right]_n$[36]. A similar insoluble product and the corresponding chelating ligand were obtained from attempted preparations of $MeSCH_2CH_2SMePd(SPh)_2$, $Ph_2PCH_2PPh_2Pd(SMe)_2$, and 1,5-$\underline{hexadiene}PtCl_2$. (The presence of the free ligand was established by the infra-red spectrum of the filtrate after the $\left[M(SR)_2\right]_n$ had been removed, and the filtrate had been concentrated).

The reactions outlined in the previous paragraph can be compared with some preliminary attempts to prepare complexes of the type $(L\text{-}L)Pt(PR_2)_2$. The reaction of $NaPMe_2$ with $Ph_2PCH_2CH_2PPh_2PtCl_2$ in ether, liberated the chelating diphosphine, $Ph_2PCH_2CH_2PPh_2$. Also, in the reaction of $Pt(PPh_3)_4$[148] with Me_2PPMe_2, all the triphenyl phosphine was liberated.

b) Mercapto Complexes of Titanium^{IV}.

Two methods were used for the preparation of the complexes $Cp_2Ti(SR)_2$ (R = Me, Ph):-

i) The reaction of Cp_2TiCl_2 with the corresponding sodium salt, NaSR[48].

ii) The reaction of Cp_2TiCl_2 with the appropriate thiol (MeSH or PhSH) in the presence of triethylamine, NEt_3[80].

Method (i) has the disadvantage that the sodium salts, NaSR, have to be completely free from metallic sodium otherwise reduction to Ti^{III} takes place. Subsequent re-oxidation by atmospheric oxygen during work up leads to complexes containing Ti-O-Ti linkages[39]. Even the use of very pure salts (as prepared by the Na/NH_3 method outlined in Section 3a, above) leads to similar products. Method (ii), which does not have this disadvantage, was

used exclusively after preliminary reactions had shown the difficulties which arose using method (i).

Preparation of $Cp_2Ti(SPh)_2$.

4.0gms. (16m.moles) of Cp_2TiCl_2 were refluxed for 3 hours in benzene containing 5.6mls. (4gms., 40m.moles) of NEt_3 and 4.5mls. (4.5gms., 44m.moles) of PhSH. The mixture was allowed to cool, and then eluted, with benzene, down a short silica column. The purple solution was concentrated until crystals separated. These crystals were recrystallised from toluene/hexane mixtures. Concentration of the original mother liquor afforded a further crop of crystals.
(Overall yield:- 4.9gms., 76%).

$Cp_2Ti(SMe)_2$ was prepared in a similar manner, though initial cooling of the reaction mixture, before introduction of the methane-thiol, and the use of a dry-ice condensor throughout were required to stop evaporation of MeSH. (Yield = 64%).

The complexes were characterised by analysis and comparison of their melting points and ^{1}Hn.m.r. spectra with the literature data[48].

Reactions (i) and (ii) failed to give $(\pi\text{-}MeC_5H_4)_2Ti(SMe)_2$,

$Cp_2Ti(SCH_2CH_2S)$, and $CpTi(SMe)_3$. ($CpTiCl_3$, which was used in the preparation of $CpTi(SMe)_3$, was obtained from the reaction of Cp_2TiCl_2 with Cl_2[134]). Black tars were obtained from the first two attempted preparations, and an intractable yellow powder was obtained from the third.

The complex $Cp_2Ti(OPh)_2$ was prepared by the method of Andra[135], and was characterised by its melting point and ^{1}Hn.m.r. spectrum.

Section 4.

Attempts to Prepare Some Other Titanium and Nickel Complexes.

Although $Cp_2Ti(C{\equiv}CPh)_2$, prepared by the reaction of $NaC{\equiv}CPh$ with Cp_2TiCl_2, has been reported[136,137], attempts to repeat the reaction almost always gave products contaminated with oxygen (See Section 3b). A complex with analytical figures very close to those required for $Cp_2Ti(Cl)C{\equiv}CPh$ was obtained in one of the preparations. (Found: C,67.2; H,5.0; Cl,14.3. $C_{18}H_{15}ClTi$ requires: C,68.7; H,4.8; Cl,11.3%).

When equimolar amounts of $Hg(C{\equiv}CPh)_2$ and Cp_2TiCl_2 were heated together in toluene at temperatures ranging from 20-110°C no reaction was observed and only starting materials were recovered. Similarly, when $Me_3SiC{\equiv}CPh$ and Cp_2TiCl_2 were heated together, in the absence of solvent, under vacuum, no exchange reaction took place. ($Hg(C{\equiv}CPh)_2$ and $Me_3SiC{\equiv}CPh$ were prepared by the reaction of $NaC{\equiv}CPh$ with $HgCl_2$ and Me_3SiCl, respectively. They were

characterised by comparison of their melting point and boiling point, respectively, with the literature values[138,139]. $Me_3SiC{\equiv}CPh$ was also characterised by its ^{1}Hn.m.r. spectrum).

The complex Cp_2TiMe_2 is reported[140] to decompose to Cp_2Ti^{II} at temperatures above 90°C, but when Cp_2TiMe_2 or Cp_2TiPh_2[141] was stirred with phenyl acetylene, $HC{\equiv}CPh$, in toluene, at 50°C or below, no reaction was observed. Heating to higher temperatures yielded an intractable red tar. It was found that when $HC{\equiv}CPh$ itself was heated in toluene above 50°C, a similar intractable red tar was observed.

The complex $Ph_2PCH_2CH_2PPh_2Ni(SPh)_2$ has been reported[133] as a red solid, prepared by treating $Ph_2PCH_2CH_2PPh_2NiCl_2$[142] with NaSPh in ethanol. When this reaction was repeated, and when a similar reaction with NaSMe was carried out, the products were found to decompose to brown powders on attempted recrystallisations from ethanol. The same type of decomposition was observed when $Ph_2PCH_2CH_2PPh_2NiCl_2$ was reacted with thiols (MeSH and PhSH) in toluene, in the presence of NEt_3.

The use of bipyridyl nickel dibromide $(C_{10}H_8N_2)NiBr_2$[143] instead of $Ph_2PCH_2CH_2PPh_2NiCl_2$ did not lead to the desired products, $(C_{10}H_8N_2)Ni(SR)_2$, by reactions analogous to those mentioned above.

Attempts to prepare biryridyl nickel bis-(phenylacetylide), $(C_{10}H_8N_2)Ni(C{\equiv}CPh)_2$, by the reaction of $NaC{\equiv}CPh$ with $(C_{10}H_8N_2)NiBr_2$ in ether and liquid ammonia were unsuccessful, as was the reaction of free bipyridyl with <u>trans</u>-$(PPh_3)_2Ni(C{\equiv}CPh)_2$[144] in toluene.

Section 5.

Preparation of Chelating Disulphide Group VI Tetracarbonyls.

The complexes have the general formula $RSCH_2CH_2SRM'(CO)_4$ (R = Me, Ph; M' = Cr, Mo, W). The complexes $MeSCH_2CH_2SMeM'(CO)_4$ were prepared, as in the literature[70], by the reaction of 2,5 dithiahexane with the Group VI hexacarbonyls, in the absence of solvent.

Preparation of $PhSCH_2CH_2SPhMo(CO)_4$.

0.25gms. (1m.mole) of $PhSCH_2CH_2SPh$ and 0.3gms. (1m.mole) of norbornadiene$Mo(CO)_4$ were stirred together in 25mls. of toluene at 50°C for 3 hours. The dark solution was filtered through a Kieselguhr pad and a clear yellow solution was obtained. The toluene was removed at reduced pressure, and the solid obtained was recrystallised from chloroform. (Yield:- 0.25gms., 55% (based on norbornadiene-$Mo(CO)_4$)).

The analogous tungsten complex was prepared in an exactly similar manner. (Yield:- 30% (based on norbornadiene-$W(CO)_4$)).

$PhSCH_2CH_2SPhMo(CO)_4$, yellow crystals; M.Pt. 120°C(Decomp.); (Found: C,47.7; H,3.0. $C_{18}H_{14}MoO_4S_2$ requires: C,47.7: H,3.1%).

$PhSCH_2CH_2SPhW(CO)_4$, yellow crystals; M.Pt. 146°C(Decomp.); (Found: C,39.8; H,2.5. $C_{18}H_{14}O_4S_2W$ requires: C,40.0; H,2.6%).

The complexes norbornadiene-$M'(CO)_4$ (M'= Cr,Mo,W) were prepared by King's method[145,146] via $(CH_3CN)M'(CO)_3$[147]. The latter complexes were not purified, but after removal of excess acetonitrile, they were used in situ.

Section 6.

Preparation of Copper^{I} Halide Complexes.

a) Preparation of 1,5cyclo-octadiene copper^{I} halides.

The title complexes, which have the general formula (1,5cyclo-octadiene-CuX)$_2$ (X= Cl,Br), were prepared by Todd's method[88]. Crystals of the complexes were filtered from the solution of $P(OPh)_3$, 1,5cyclo-octadiene, and methanol, and washed rapidly with 10mls. of a cold (0°C), 5% solution of 1,5cyclo-octadiene in methanol. The crystals were not dried before they were reacted with $RSCH_2CH_2SR$ (Section 6b) and $Cp_2Ti(SR)_2$ (Section 7b), as it was found that successive washings and drying of the complexes, by pumping in vacuo, removed some of the co-ordinated 1,5cyclo-octadiene.

b) Preparation of chelating disulphide complexes of copper^{I} halides.

These complexes have the general formula $(RSCH_2CH_2SRCuX)_n$ (R = Me, Ph; X = Cl, Br).

Preparation of $(MeSCH_2CH_2SMeCuCl)_n$.

1.7gms. (10m.moles) of $CuCl_2.2H_2O$ were dissolved in 30mls. methanol. 3.1gms. (10m.moles) of $P(OPh)_3$ were added followed immediately by 3mls. of 2,5 dithiahexane, and the flask was shaken to mix the reactants. The solution, initially dark brown, was almost colourless after standing at room temperature for 12 hours. On addition of a small volume of pentane (5mls.) white crystals began to separate. After standing for a further 24 hours, the crystals were filtered off under nitrogen, washed with pentane, and dried at room temperature in vacuo. Although the crystals seemed stable when precipitating from the 2,5 dithiahexane rich mother liquor, they decomposed in air, when dry.

The corresponding bromide complex was prepared in a similar manner.

$(MeSCH_2CH_2SMeCuCl)_n$, white crystals; M.Pt. 148-150°C; (Found: C, 20.6; H, 4.6; Cl, 16.8. $(C_4H_{10}CuClS_2)_n$ requires: C, 21.9; H, 4.6; Cl, 16.1%).

$(MeSCH_2CH_2SMeCuBr)_n$, white crystals; M.Pt.161-2°C; (Found: C,17.0; H,3.5; Br,31.1. $(C_4H_{10}BrCuS_2)_n$ requires: C,18.0; H,3.8; Br,30.0%).

Preparation of $(PhSCH_2CH_2SPhCuCl)_n$.

1.7gms. (10m.moles) of $CuCl_2.2H_2O$ were dissolved in 30mls. methanol and 10mls. T.H.F.. 3.1gms. (10m.moles) of $P(OPh)_3$ were added followed by 2.4gms. (10m.moles) of $PhSCH_2CH_2SPh$ dissolved in 10mls. T.H.F.. The mixture was shaken and allowed to stand for 12 hours. The solution gradually became much lighter in colour, and white crystals began to separate out. The crystals were filtered off, washed with toluene and pentane, and dried in vacuo at room temperature. Compared with the methyl derivatives, this complex was found to be very air stable. The bromide complex was similarly prepared and was also found to be air stable.

$(PhSCH_2CH_2SPhCuCl)_n$, white crystals; M.Pt. 108°C; (Found: C,49.6; H,4.1; Cl,11.1. $(C_{14}H_{14}ClCuS_2)_n$ requires: C,48.8; H,4.1; Cl,10.3%).

$(PhSCH_2CH_2SPhCuBr)_n$, white crystals; M.Pt. 140°C; (Found: C,43.0; H,3.7; Br,19.9. $(C_{14}H_{14}BrCuS_2)_n$ requires: C,43.2; H,3.6; Br,20.6%).

The complexes $(RSCH_2CH_2SRCuX)_n$ were found to be insoluble in all solvents tried, after the complexes had been filtered off and dried. Recrystallisation was therefore not possible and, although the crystals were well formed, this probably accounts for the rather inaccurate data given on the previous pages. Insolubility also precluded the determination of molecular weights, but this insolubility itself probably indicates aggregation in the solid state, i.e. $n \geqslant 2$, in the above formulation.

Attempts to prepare $(RSCH_2CH_2SRCuX)_n$ by the reaction of the chelating disulphide with $(1,5\underline{\text{cyclo-octadiene}}\text{-}CuX)_2$ (Section 6a) proved unsuccessful, giving products which were contaminated with cuprous or cupric halides, as could be inferred from the analytical figures for the products obtained.

Section 7.

Reactions of $Cp_2Ti(SR)_2$ With Transition Metal Complexes.

a) Reactions of $Cp_2Ti(SR)_2$ (R = Me, Ph) with norbornadiene-$M'(CO)_4$ (M' = Cr, Mo, W).

These reactions were carried out in toluene at room temperature. For a given Group VI metal, reactions were much faster when R = Me than when R = Ph.

Preparation of $Cp_2Ti[SMe]_2Mo(CO)_4$.

1gm. (3.6m.moles) of $Cp_2Ti(SMe)_2$ were stirred in 50mls. toluene with 1gm. (3.3m.moles) of norbornadiene-$Mo(CO)_4$. The solution turned from purple to deep blue after 30mins., but the reaction mixture was stirred for a further 6 hours. The reaction mixture was filtered. The residue was washed with a 10mls. portion of toluene, and several times with n-hexane. The dark blue solid was crystallised rapidly by dissolving in methylene chloride, filtering, adding methylcyclohexane, and removing the methylene chloride at

room temperature, under reduced pressure. The small, dark blue crystals were washed with n-hexane and dried in vacuo at room temperature. Somewhat larger crystals were obtained by recrystallisation from benzene, in which the product was found to be slightly soluble. Great care was required to exclude all air from the benzene solutions while a much slower precipitation, than that mentioned above, proceeded. A certain amount of decomposition always occurred however, and the larger crystals had to be removed manually from the decomposition products, after filtration. (Yield (after recrystallisation from methylene chloride/methylcyclohexane):- 1.3gms., 60% (based on norbornadiene-$Mo(CO)_4$)).

$Cp_2Ti[SMe]_2Mo(CO)_4$, blue crystals; does not decompose below 300°C; (Found: C,39.7; H,3.3; S,12.9; Ti,9.2; Mo,20.4. $C_{16}H_{16}MoO_4S_2Ti$ requires: C,40.0; H,3.4; S,13.4; Ti,9.9; Mo,19.9%).

The analogous chromium and tungsten complexes were similarly prepared, but the reaction proceeded much more slowly. Stirring was continued for 36 and 27 hours for the Cr and W complexes, respectively. The complexes were again recrystallised from methylene chloride/methylcyclohexane mixtures, but the Cr complex was too unstable in solution to carry out a slow recrystallisation from benzene.

(Yields:- Cr = 30%, W = 72% (based on norbornadiene-M'$(CO)_4$)

$Cp_2Ti\left[SMe\right]_2Cr(CO)_4$, dark green crystals; does not decompose below 300°C; (Found: C,43.9; H,3.8; S,14.3; Ti, 11.3; Cr,12.0. $C_{16}H_{16}CrO_4S_2Ti$ requires: C,43.9; H,3.7; S,14.7; Ti,11.0; Cr,12.1%).

$Cp_2Ti\left[SMe\right]_2W(CO)_4$, blue crystals; does not decompose below 300°C; (Found: C,34.0; H,2.9; S,11.6; Ti,7.9. $C_{16}H_{16}O_4S_2TiW$ requires: C,33.8; H,2.8; S,11.2; Ti,8.4%).

Similar preparations yielded $Cp_2Ti\left[SPh\right]_2Mo(CO)_4$ (20% after 30 hours) and $Cp_2Ti\left[SPh\right]_2W(CO)_4$ (25% after 90hours) but none of the corresponding chromium complex was obtained after 7 days under the same conditions. On heating the last mentioned reaction mixture, only black decomposition products were observed.

$Cp_2Ti\left[SPh\right]_2Mo(CO)_4$, blue crystals; does not decompose below 300°C; (Found: C,51.0; H,3.3; S,10.0; Ti,7.5; Mo,16.0. $C_{22}H_{20}MoO_4S_2Ti$ requires: C,51.4; H,3.6; S,10.3; Ti,7.9; Mo,15.8%).

$Cp_2Ti\left[SPh\right]_2W(CO)_4$, blue crystals; does not decompose below 300°C; (Found: C,45.0; H,3.0; S,9.4; Ti,6.9. $C_{22}H_{20}O_4S_2TiW$ requires: C,45.2; H,2.9; S,9.3; Ti,6.2%).

The complexes prepared were stable long enough in solution to obtain their solution infra-red and visible/u.v.

spectra in chlorinated alkyl solvents such as chloroform and methylene chloride. The longer time required to run variable temperature ^{1}Hn.m.r. spectra necessitated the use of chlorobenzene as solvent, in which the complexes were found to be stable for much longer periods.

Ebullioscopic molecular weight determinations of the complexes, in acetone, indicated that the complexes were monomeric in solution, although reproducible results (to within 10%) were not obtained because of initial insolubility and subsequent decomposition of the complexes.

b) Reactions of $Cp_2Ti(SR)_2$ with (1,5cyclo-octadiene-CuX)$_2$.

These reactions were carried out at room temperature, in toluene. The reactions were again found to be much faster for R = Me than for R = Ph, but seemed independent of whether X = Cl or X = Br. Quantitative yields of the products were obtained.

Preparation of $(Cp_2Ti[SMe]_2CuCl)_n$.

0.9gms. (3.2m.moles) of $Cp_2Ti(SMe)_2$ were dissolved in 50mls. toluene. When dissolution was complete, 0.7gms. (1.5m.moles) of (1,5cyclo-octadieneCuCl)$_2$ (Section 6a) were added. Stirring at room temperature was continued for 4 hours. The black solid which separated out was

filtered off, washed with toluene and pentane, and dried in *vacuo* at room temperature.

The product was found to be insoluble in all solvents tried, hence, it could not be crystallised, and its molecular weight could not be determined.

$(Cp_2Ti[SMe]_2CuCl)_n$, black powder; M.Pt. 170°C(Decomp.); (Found: C,39.5; H,4.6; Cl,9.5; S,17.0; Ti,11.9; Cu,17.7. $(C_{12}H_{16}ClCuS_2Ti)_n$ requires: C,38.9; H,4.4; Cl,9.6; S,17.3; Ti,12.9; Cu,17.1%).

The following complexes were prepared in a similar manner. (Where R = Ph, the reaction time was 18 hours):-

$(Cp_2Ti[SMe]_2CuBr)_n$, black powder; decomposes slowly above 186°C; (Found: C,33.7; H,3.8; Br,20.4; Cu,14.8; S,15.3; Ti,11.3. $(C_{12}H_{16}BrCuS_2Ti)_n$ requires: C,34.7; H,3.9; Br,19.2; Cu,15.3; S,15.4; Ti,11.4%).

$(Cp_2Ti[SPh]_2CuCl)_n$, brown powder; decomposes slowly above 135°C; (Found: C,52.4; H,3.9; Cu,12.0; S,13.7; Ti,10.3; Cl,7.4. $(C_{22}H_{20}ClCuS_2Ti)_n$ requires: C,53.4; H,4.0; Cu,12.9; S,13.0; Ti,9.7; Cl,7.2%).

$(Cp_2Ti[SPh]_2CuBr)_n$, brown powder; decomposes slowly above 174°C; (Found: C,47.5; H,3.6; Cu,11.7; Br,15.3; S,11.6 Ti,9.0. $(C_{22}H_{20}BrCuS_2Ti)_n$ requires: C,48.9; H,3.7; Cu,11.8;

Br,14.8; S,11.9; Ti,8.9%).

The direct reaction of $Cp_2Ti(SR)_2$ with CuX_2 and $P(OPh)_3$ in methanol, gave, instead of the desired products, an almost quantitative yield of Cp_2TiX_2 which precipitated from the reaction mixture, and was filtered off.

All of the complexes $(Cp_2Ti[SR]_2CuX)_n$ were found to react rapidly with $P(\underline{n}\text{-}C_4H_9)_3$ in benzene to liberate $Cp_2Ti(SR)_2$, which was characterised by its ^{1}Hn.m.r. spectrum, after extraction of the complex from the reaction mixture, with benzene, as well as a tarry residue which was not characterised.

c) Miscellaneous Reactions of $Cp_2Ti(SR)_2$.

i) Reaction of $Cp_2Ti(SMe)_2$ with $(PhCN)_2PdCl_2$.

0.8gms. (2.9m.moles) of $Cp_2Ti(SMe)_2$ were stirred in 40mls. toluene with 1.0gm. (2.6m.moles) $(PhCN)_2PdCl_2$. After 1 hour, a precipitate was observed, but stirring at room temperature was continued for a further 2 hours. The solid was filtered off, dried, and extracted with methylene chloride. On removal of the methylene chloride, Cp_2TiCl_2 was obtained. The part insoluble in methylene chloride was found to be insoluble in all solvents tried, and, although consistent (to within 5%) analytical figures

for carbon and sulphur, were not obtained from several different reactions, the complex is thought to be $\left[Pd(SMe)_2\right]_n$.

$Cp_2Ti(SMe)_2$ did not react with $(PhCN)_2PtCl_2$ or $(PPh_3)_2NiCl_2$[149] under similar conditions.

ii) Reaction of $Cp_2Ti(SMe)_2$ with $Mn(CO)_5Br$.

0.8gms. (3.2m.moles) of $Mn(CO)_5Br$ and 1gm. (3.7m.moles) of $Cp_2Ti(SMe)_2$ were stirred in refluxing ethanol for $2\frac{1}{2}$ hours. (There was no reaction in either toluene or cold ethanol). The solution became much lighter and a pale yellow solid separated. The mixture was filtered hot. The residue had an infra-red spectrum (4000-600cm.$^{-1}$) almost identical with that of the complex(s) obtained when $Cp_2Ti(Cl)SMe$[48] is refluxed in ethanol. The solvent was removed from the filtrate, and the infra-red spectrum of the solid thus obtained was the same as that of $(Mn(CO)_3SMe)_4$[106b]. An analytically pure sample of this complex was not obtained: all samples, even after recrystallisation from ethanol, contained small percentages of titanium.

iii) Reaction of $Cp_2Ti(SPh)_2$ with $Ru(CO)_3Cl_2$T.H.F.[150].

0.8 gms. (2.4m.moles) of $Ru(CO)_3Cl_2$T.H.F. and 1.2gms. (3.5m.moles) of $Cp_2Ti(SPh)_2$ were stirred in 50mls. toluene for 24 hours at room temperature. A red precipitate was

observed and the mixture was filtered. The precipitate was found to be Cp_2TiCl_2. The volume of the filtrate was reduced and more Cp_2TiCl_2 precipitated out. On complete removal of the solvent, a red oil was obtained. This oil contained carbonyl groups, but the complexes could not be separated. The infra-red spectrum of the oil did, however, indicate the presence of $\left[(OC)_3RuSPh\right]_n$[151]. (From a similar reaction between $Fe_3(CO)_{12}$ and $Cp_2Ti(SPh)_2$, the complex $\left[(OC)_3FeSPh\right]_2$ has been obtained[152]).

Reactions of $Cp_2Ti(SR)_2$ with 2-methoxyethanol/CO/$RuCl_3.3H_2O$ solutions[153] (at room temperature and at reflux temp.) also gave Cp_2TiCl_2 and intractable red tars with infra-red spectra similar to that noted above.

iv) Reaction of $Cp_2Ti(SPh)_2$ with $C_4H_2O_3Fe(CO)_4$. ($C_4H_2O_3Fe(CO)_4$ = maleic anhydride-$Fe(CO)_4$[155]).

1.2gms. (4.5m.moles) of $C_4H_2O_3Fe(CO)_4$ and 0.8gms. (2m.moles) of $Cp_2Ti(SPh)_2$ were stirred at room temperature in toluene and no reaction was observed. The mixture was then heated to reflux temperature for 3 hours, cooled, filtered, and the toluene was removed from the filtrate leaving $\left[FeCp(CO)_2\right]_2$, which was characterised by its infra-red spectrum and melting point[154].

Section 8.

Reactions of $(L\text{-}L)M(SR)_2$ With Transition metal complexes.

All the reactions of $(L\text{-}L)M(SR)_2$ (L-L = 1,2 bis-diphenylphosphino ethane, o-phenylene bis-diethylarsine; M = Pd, Pt; R = Me, Ph) were carried out at room temperature in toluene. Reaction times were adjusted to give quantitative yields of the desired products, since their insolubility led to problems of separation from the rather insoluble $(L\text{-}L)M(SR)_2$.

a) Reactions of $(L\text{-}L)M(SR)_2$ with norbornadiene-$M'(CO)_4$. Preparation of $Ph_2PCH_2CH_2PPh_2Pt[SMe]_2Mo(CO)_4$.

0.68gms. (1m.mole) of $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$ and 0.30gms. (1m.mole) of norbornadiene-$Mo(CO)_4$ were stirred at room temperature in 50mls. toluene for 50 hours. The reaction mixture was filtered, washed with toluene and pentane, and carefully dried at room temperature, in vacuo.

The product was found to be insoluble in all but the most polar solvents, and in these, decomposition was rapid. The product was therefore characterised without further purification. This preparation, and those of the related complexes, listed below, were repeated until consistent analytical figures were obtained.

$\underline{Ph_2PCH_2CH_2PPh_2Pt}\left[SMe\right]_2\underline{Mo(CO)_4}$, yellow powder; decomposes without melting at 160°C; (Found: C,43.5; H,3.6; S,6.3; P,7.4. $C_{32}H_{30}MoO_4P_2PtS_2$ requires: C,42.9; H,3.4; S,7.2; P,6.9%).

The following complexes were prepared in a similar manner; reaction times are given in parentheses:-

$\underline{Ph_2PCH_2CH_2PPh_2Pd}\left[SMe\right]_2\underline{Cr(CO)_4}$, (120 hours); yellow powder; decomposes without melting at 190°C; (Found: C,50.2; H,4.1: S,7.3: P,9.2. $C_{32}H_{30}CrO_4P_2PdS_2$ requires: C,50.5: H,4.0; S,8.4; P,9.2%).

$\underline{Ph_2PCH_2CH_2PPh_2Pd}\left[SMe\right]_2\underline{Mo(CO)_4}$, (30 hours); brown powder; M.Pt. 190-3°C (Decomp.); (Found: C,47.5; H,4.1. $C_{32}H_{30}MoO_4P_2PdS_2$ requires: C,47.6; H,3.8%).

$\underline{Ph_2PCH_2CH_2PPh_2Pd}\left[SMe\right]_2\underline{W(CO)_4}$, (50 hours); brown powder; M.Pt. 161-4°C; (Found: C,42.7; H,3.8: S,7.0; P,6.4. $C_{32}H_{30}O_4P_2PdS_2W$ requires: C,42.9, H,3.4; S,7.2; P,6.9%).

$Ph_2PCH_2CH_2PPh_2Pt[SMe]_2Cr(CO)_4$, (130 hours); yellow powder; decomposes without melting above 120°C; (Found: C,45.9; H,3.9; S,7.4; P,7.9. $C_{32}H_{30}CrO_4P_2PtS_2$ requires: C,45.1; H,3.5: S,7.5: P,7.3%).

$Ph_2PCH_2CH_2PPh_2Pt[SMe]_2W(CO)_4$, (60 hours); yellow powder; M.Pt. 170-4°C (Decomp.); (Found: C,39.2; H,2.9; S,6.1. $C_{32}H_{30}O_4P_2PtS_2W$ requires: C,39.2; H,3.1; S,6.5%).

$C_6H_4(AsEt_2)_2Pd[SMe]_2Mo(CO)_4$, (2 hours); brown powder; colour change above150°C, does not melt below 230°C; (Found: C,31.4; H,3.9. $C_{20}H_{30}As_2MoO_4PdS_2$ requires: C,32.2; H,4.0%).

$C_6H_4(AsEt_2)_2Pd[SPh]_2Mo(CO)_4$, (4 hours); brown powder; M.Pt. 117-120°C (Decomp.) (Found: C,41.0; H,3.9. $C_{30}H_{34}As_2MoO_4PdS_2$ requires: C,42.0; H,3.9%).

The much faster rate of reaction in reactions involving the chelating diarsine complexes is probably due to their greater solubility in toluene.

The complexes $Ph_2PCH_2CH_2PPh_2Pd[SPh]_2Mo(CO)_4$ and $Ph_2PCH_2CH_2PPh_2Pt[SPh]_2Mo(CO)_4$ were not obtained analytically pure, but were characterised by the similarity of their infra-red spectra with other members of the series.

The complexes $Ph_2PCH_2CH_2PPh_2M\left[SPh\right]_2M'(CO)_4$ (M = Pd, Pt; M' = Cr, W) and $C_6H_4(AsEt_2)_2Pd\left[SR\right]_2M'(CO)_4$ (R = Me, Ph; M' = Cr, W) were not obtained because of extremely long reaction times and/or instability of the desired products.

b) Reactions of $Ph_2PCH_2CH_2PPh_2M(SR)_2$ with $(PhCN)_2MCl_2$ (M = Pd, Pt; R = Me, Ph).

Preparation of $Ph_2PCH_2CH_2PPh_2Pt\left[SMe\right]_2PdCl_2$.

0.175gms. (0.04m.mbles) of $(PhCN)_2PdCl_2$ were added to a suspension of 0.316gms. (0.04m.moles) of $Ph_2PCH_2CH_2PPh_2Pt(SMe)_2$ in toluene. The mixture was stirred until the supernatent liquid became colourless (48 hours). The solid was filtered off, washed with toluene and pentane, and dried in vacuo. The quantitative yield of product obtained could not be crystallised because of its insolubility.

$Ph_2PCH_2CH_2PPh_2Pt\left[SMe\right]_2PdCl_2$, orange/brown powder; M.Pt. 226-230°C; (Found: C,39.8; H,3.5; S,6.8; P,6.7; Cl,7.8. $C_{28}H_{30}Cl_2P_2PdPtS_2$ requires: C,38.9; H,3.5; S,7.4; P,7.2; Cl,8.8%).

A similar reaction gave:-

$Ph_2PCH_2CH_2PPh_2Pd\left[SMe\right]_2PdCl_2$, brown powder; M.Pt. 194-9°C;

(Found: C,44.3: H,4.3; P,7.9. $C_{28}H_{30}Cl_2P_2Pd_2S_2$ requires: C,43.3; H,3.9; P,8.0%).

No reaction was observed between $Ph_2PCH_2CH_2PPh_2M(SPh)_2$ (M = Pd, Pt) and $(PhCN)_2PdCl_2$, or between $Ph_2PCH_2CH_2PPh_2M(SMe)_2$ (M = Pd, Pt) and $(PhCN)_2PtCl_2$. The reaction between $Ph_2PCH_2CH_2PPh_2Pd(SMe)_2$ and 1,5hexadiene-$PtCl_2$, gave complexes which could not be characterised.

Section 9.

Reactions of Metal Dichloride Complexes as Ligands.

The metal dichloride complexes which were used as potential ligands were $Ph_2PCH_2CH_2PPh_2MCl_2$ (M = Ni, Pd, Pt).

Preparation of $Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$.

A suspension of 0.3gms. of $Ph_2PCH_2CH_2PPh_2PdCl_2$ and excess (0.5gms.) of $(PhCN)_2PdCl_2$ were stirred in 40mls. toluene at room temperature for 72 hours. The solid was filtered off, washed with toluene and pentane, and dried in vacuo.

$Ph_2PCH_2CH_2PPh_2Pd\left[Cl\right]_2PdCl_2$, light brown powder; M.Pt. 201-6°C (Decomp.); (Found: C,41.7; H,3.2; Cl,18.3. $C_{26}H_{24}Cl_4P_2Pd_2$ requires: C,41.5; H,3.2; Cl,19.0%).

The reactions of $Ph_2PCH_2CH_2PPh_2MCl_2$ (M = Ni, Pt) with $(PhCN)_2PdCl_2$ gave $PdCl_2$ and $Ph_2PCH_2CH_2PPh_2MCl_2$. ($PdCl_2$ was left as a residue after all the $Ph_2PCH_2CH_2PPh_2MCl_2$ had been extracted from the reaction mixture with dimethylformamide).

The reactions of $Ph_2PCH_2CH_2PPh_2MCl_2$ (M = Ni, Pd, Pt) with $(PhCN)_2PtCl_2$, under similar conditions, yielded only starting materials.

Section 10.

Attempted Preparations of Some Transition Metal-Silicon Complexes.

These reactions were carried out in an attempt to prepare silicon bridged transition metal complexes.

The salts $NaCo(CO)_4$, $NaCpFe(CO)_2$, and $NaMn(CO)_5$ were prepared by reduction of the corresponding dinuclear metal carbonyl complex with a Na/Hg amalgam, as described by King[156]. Solutions of chlorosilanes were made up in a drybox to avoid hydrolysis.

a) Reaction of $NaCo(CO)_4$ with Me_2SiCl_2.

A solution of 0.58gms. (3m.moles) of $NaCo(CO)_4$ in 20mls. T.H.F. was added dropwise to a stirred solution of 2m.moles Me_2SiCl_2 in 30mls. T.H.F. at room temperature. After stirring for a few minutes, the solution became blue/green and a green solid was observed. The solvent was removed under reduced pressure, and a green tar remained. Sublimation, under reduced pressure (0.001mm.Hg) at room temperature, gave a very small amount of an orange solid

which was characterised, by its infra-red spectrum, as $Hg(Co(CO)_4)_2$[157]. Continued sublimation did not yield any further products, and the infra-red spectrum of the tar, in the carbonyl region, showed only weak peaks which could be assigned to $Hg(Co(CO)_4)_2$. On addition of water to a small amount of the green tar, a pink aqueous layer was observed, indicative of the presence of cobaltous chloride hexahydrate, $CoCl_2.6H_2O$.

A small amount of T.H.F. was added to the green tar, and gave a blue solution (again, indicative of the presence of $CoCl_2$). This blue solution was decanted off and the T.H.F. was removed. The sticky blue solid obtained was pumped on, under vacuum, for several days, but analytically pure$CoCl_2$ was not obtained, although the low carbon and high chlorine and cobalt values suggested that $CoCl_2$ was present.

The presence of Si-CH_3 groups in the residual green tar was indicated by the characteristic bands at 1300cm.$^{-1}$ (approximately) in its infra-red spectrum[158].

b) <u>Reaction of $PhMeSiH_2$ with $Co_2(CO)_8$.</u>

$PhMeSiH_2$ was prepared by the reaction of $LiAlH_4$ on $PhMeSiCl_2$[159]. 1.39gms. (4.1m.moles) of $Co_2(CO)_8$ and 1gm. (8.2m.moles) of $PhMeSiH_2$ were stirred together without

solvent, and rapid evolution of gas took place. After 15 minutes, gas evolution had ceased, and the infrared carbonyl spectrum of the reaction mixture differed from that of $Co_2(CO)_8$. Attempts to purify the products, by chromatography and extraction with various solvents, were unsuccessful. When the mixture was sublimed in vacuo (0.001mm.Hg) at room temperature, small amounts of $Co_2(CO)_8$ and larger amounts of $Co_4(CO)_{12}$ were obtained. A large amount of tarry residue was left after sublimation, and although its infra-red spectrum showed strong peaks due to carbonyl groups, no further products could be extracted.

A similar reaction was carried out by allowing $HCo(CO)_4$ to distill onto $PhMeSiH_2$ in a vacuum line, but again, $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were the only products which could be extracted. ($HCo(CO)_4$ was prepared by treating $Co_2(CO)_8$ with pyridine followed by H_2SO_4 [160])

c) Preparation of $ClMe_2SiCo(CO)_4$.

1gm. of $Co_2(CO)_8$ and excess (1ml.) of Me_2SiHCl were mixed together without solvent at room temperature. Rapid evolution of gas took place, and a light brown solid was observed. After the gas evolution had ceased, the solid was dissolved in pentane and cooled to -78°C. A white crystalline solid separated out, and was removed by filtration of the cold solution. The product was further

purified by sublimation in <u>vacuo</u> (0.01mm.Hg) at room temperature.

$ClMe_2SiCo(CO)_4$, M.Pt. 45°C, shows $\nu C\equiv O$ at 2098, 2040, 2015, and 2002cm.$^{-1}$ in an intensity ratio which is consistent with approximate C_{3v} symmetry where the E band is split since only 2 of the substituents at silicon are the same[161]. Its ^{1}Hn.m.r. spectrum shows a singlet at 9.2τ (relative to internal T.M.S. at 10.0τ) with small side bands due to ^{29}Si-H coupling. ($J_{^{29}Si-H}$ = 3.2Hz).

When $ClMe_2SiCo(CO)_4$ was added to dry, freshly distilled T.H.F. or diethyl ether, it decomposed to $CoCl_2$ (Section 10a), very rapidly. Since T.H.F. and diethyl ether are virtually the only solvents that can be used for the preparation of the sodium salts of the metal carbonyls, the decomposition of $ClMe_2SiCo(CO)_4$ in these solvents presented experimental difficulties, as it was intended to react $ClMe_2SiCo(CO)_4$ with the metal carbonyl anions, $Co(CO)_4^-$ etc..

In the following reactions, (d) and (e), $NaCo(CO)_4$, $NaMn(CO)_5$, and $NaCpFe(CO)_2$ were prepared in T.H.F. which was then removed, and toluene was added to the dry salts. Great care has to be taken to exclude air from the dry salts as they are extremely pyrophoric.

d) Reaction of $ClMe_2SiCo(CO)_4$ with $NaCo(CO)_4$.

0.9gms. (3.4m.moles) of $ClMe_2SiCo(CO)_4$ were added to a suspension of 1gm. (3.4m.moles) of $NaCo(CO)_4$ in 20mls. toluene. After stirring for 1 hour at room temperature, no change was observed in the number or positions of the carbonyl peaks in the infra-red spectrum of the solution. The temperature was increased to 60°C and a gradual darkening of the solution followed. After 2 hours at this temperature, the solid obtained, after removal of the T.H.F., was transferred, in a drybox flushed with nitrogen, to a sublimation apparatus. The products obtained by fractional sublimation were identified by their infra-red spectra as $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $ClMe_2SiCo(CO)_4$. An infra-red spectrum of a T.H.F. solution of the residual material indicated the presence of unreacted $NaCo(CO)_4$. Heating the reaction mixture for longer periods and at higher temperatures yielded only larger amounts of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ together with a silicon containing tar.

A similar reaction between $NaMn(CO)_5$ and $ClMe_2SiCo(CO)_4$ at room temperature gave only $Mn_2(CO)_{10}$ and unreacted starting materials.

e) Reaction of $NaCpFe(CO)_2$ with $ClMe_2SiCo(CO)_4$.

0.54gms. (2m.moles) of $ClMe_2SiCo(CO)_4$ were added to a suspension of 0.5gms. (2.5m.moles) of $NaCpFe(CO)_2$ in 10mls. toluene, and the mixture was stirred at room temperature. After 30 minutes the carbonyl stretching region of the solution infra-red spectrum had changed noticeably. The toluene was removed at reduced pressure, and a small amount of unreacted $ClMe_2SiCo(CO)_2$ was recovered by sublimation. The residue was extracted with toluene and, on removal of the toluene, a thick yellow oil was obtained. The large number of peaks observed in the carbonyl stretching region of the infra-red spectrum of this oil, indicated the presence of a mixture of products. $Si-CH_3$ groups were also present in this oil which could not be separated, by chromatography on a silica column, into its pure components.

f) Reaction of Me_2SiHCl with $NaCpFe(CO)_2$.

A solution of 1gm. of $NaCpFe(CO)_2$ in 30mls. of T.H.F. was cooled to 0°C and 1gm. of Me_2SiHCl (excess) was added. Immediate precipitation of a white solid was observed. The reaction was allowed to continue for 30 minutes, then the T.H.F. was removed under reduced pressure, leaving a brown oil and a small amount of white solid (NaCl). Fractional distillation of the brown oil under vacuum, yielded a yellow oil which was characterised, by its infra-red spectrum as $HSiMe_2CpFe(CO)_2$. (The infra-red spectrum is in

complete agreement with that recently published for this complex[121]).

When $HSiMe_2CpFe(CO)_2$ was heated to room temperature or above, it decomposed to yield $\left[CpFe(CO)_2\right]_2$.

Similar reactions with $NaCo(CO)_4$ and $NaMn(CO)_5$ instead of $NaCpFe(CO)_2$, yielded only $Co_4(CO)_{12}$ and $Mn_2(CO)_{10}$, and there is no evidence that any Co/Si or Mn/Si complexes were formed.

g) Reaction of $CpFe(CO)_2SiMe_2H$ with $Co_2(CO)_8$.

Since $CpFe(CO)_2SiMe_2H$ was found to be rather thermally unstable, it was prepared in situ. 0.6gms. (3m.moles) of $NaCpFe(CO)_2$ in 50mls. T.H.F. were added to 0.29gms. (3m.moles) of Me_2SiHCl in 10mls. T.H.F. at 0°C. After 30 minutes the mixture was filtered and the T.H.F. was removed from the filtrate at 0°C. 5mls. of pentane were added to the brown oil obtained. On addition of 0.51gms. (1.5m.moles) of $Co_2(CO)_8$ to this solution, gas was evolved. After 3 hours, the mixture was cooled to -78°C and a red/brown solid precipitated out. This solid was filtered off and dried. It showed a very complex infra-red carbonyl stretching frequency pattern, similar to that of the yellow oil from the reaction of $NaCpFe(CO)_2$ with $ClMe_2SiCo(CO)_4$ (Section 10e). Again, attempts to separate this solid into its components,

by chromatography and sublimation, were unsuccessful. The mass spectrum (probe temperature = 22°C) of a sample of this crude product showed $\left[CpFe(CO)_2\right]_2$, Cp_2Fe, and $CpFe(CO)\left[CO\right]_2Co(CO)_3$ as the only transition metal containing species present. At higher probe temperature (160°C) the mass spectrum showed only $\left[CpFe(CO)_2\right]_2$, Cp_2Fe, and $Co_4(CO)_{12}$

Section 11.

Attempted Preparations of Cobalt-Titanium Complexes.

a) Reaction of $NaCo(CO)_4$ with Cp_2TiCl_2.

0.6gms. (2.4m.moles) of Cp_2TiCl_2 were added to a solution of 1gm. (5m.moles) of $NaCo(CO)_4$ in 50mls. T.H.F.. No reaction took place at room temperature, but on heating the reaction mixture to 50°C, the solution became lighter in colour. Stirring at this temperature was continued for 3 hours, then the mixture was filtered. The solution showed a complicated infra-red carbonyl stretching frequency pattern. On removal of the T.H.F., a sticky solid was obtained, which showed only 2 carbonyl peaks. Toluene (5mls.) was added and the mixture was shaken and filtered. The residue was a light brown titanium containing powder which contained no carbonyl groups. When the toluene was removed from the filtrate, an oil was obtained which was characterised, by its infra-red spectrum, as $CpCo(CO)_2$[154b].

This reaction was repeated in the presence of varying

amounts of PPh_3, but the products in these reactions were $Ph_3PCo(CO)_3Co(CO)_3PPh_3$ (characterised by its infra-red spectrum[124]) and an intractable yellow powder.

Similar reactions of $Cp_2TiCl\text{-}O\text{-}ClTiCp_2$[39] and $\left[Cp\ Ti^{III}Cl\right]_2$[39] with $NaCo(CO)_4$ in T.H.F. were found to give $CpCo(CO)_2$ as the only carbonyl containing product.

b) Reaction of $HCo(CO)_4$ with Cp_2TiMe_2.

$HCo(CO)_4$[160] was distilled under vacuum onto 0.1gms of Cp_2TiMe_2 in 20mls. T.H.F.. The solution was allowed to heat up to room temperature and the reaction mixture was stirred for 12 hours at this temperature. Stirring was carried out in the dark, as Cp_2TiMe_2 is light sensitive. The solution was then cooled to -78°C and an infra-red spectrum of the volatile products indicated the presence of methane and carbon monoxide.

The T.H.F. was removed, and on extraction of the yellow powder, with toluene, $CpCo(CO)_2$ was observed. When the reaction was repeated at 0°C and below, the same products were observed.

REFERENCES.

1. B.J. Aylett and J.M. Campbell, Chem.Comm., 1965,217.
2. D.J. Patmore and W.A.G. Graham, Inorg.Chem., 1966,5,1586.
3. D.J. Cardin, S.A. Keppie, B.M. Kingston, and M.F. Lappert Chem.Comm., 1967,1035.
4. A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolabova, and M.Ya Zakharova, Izvest. Akad. Nauk SSSR., Ser. khim., 1965,1122.
5. J.M. Burtlich and S.W. Ulmer, J.Organometallic Chem., 1969,19,P21.
6. W. Jetz and W.A.G. Graham, J.Amer.Chem.Soc., 1967,89,2773.
7. A.G. Massey, A.J. Park, and F.G.A. Stone, J.Amer.Chem.Soc., 1963,85,2021.
8. H. Schumann, O. Stelzer, and W.Gick, Angew. Chem. Internat. Edn., 1969,8,271.
9. E.W. Abel, J.P. Crow, and S.M. Illingworth, J.Chem.Soc. (A), 1969,1631.
10. R.S. Nyholm and K. Vrieze, J.Chem.Soc., 1965,5337.
11. J. Lewis and S.B. Wild, J.Chem.Soc.(A), 1966,69.
12. J.M. Burtlich, Chem.Comm., 1968,887.
13. S.V. Dighe and M. Orchin, J.Amer.Chem.Soc. 1964,86,3895.

14. F. Glockling and K.A. Hooton, J.Chem.Soc.(A), 1967,1066.

15. J. Chatt, C. Eaborn, and P.N. Kapoor, J.Organometallic Chem., 1968,13,P21.

16. K.K. Joshi and P.L. Pauson, Z.Naturforsch., 1962,17b,565.

17. A.N. Nesmeyanov, N.E. Kolobova, K.N. Anisimov, and I.S. Kolomnikov, Izvest.sibirsk.Otdel.Akad.Nauk, Ser.khim.Nauk, 1963,194.

18. K. Yasufuku and H. Yamazaki, Bull.Chem.Soc.Japan. 1969,42,3099.

19. B.C. Benson, R. Jackson, K.K. Joshi, and D.T. Thompson, Chem.Comm., 1968,1506.

20. D.C Bradley and A.S. Kasennally, Chem.Comm., 1968,1430.

21. H. Köpf and K.H. Räthlein, Angew.Chem. Internat.Edn., 1969,8,980.

22.a A.R. Dias and M.L.H. Green, Chem.Comm., 1969,962.

b. M.L.H. Green, personal communication.

23. L.F. Dahl and R.E. Rundle, Acta Cryst.,1963,16,419.

24. L.F. Dahl, E. Ishishi, and R.E. Rundle, J.Chem.Phys., 1957,26,1750

25. Y.T. Strucktov, K.N. Anisimov, O.P. Osipova, N.E. Kolobova, and A.N. Nesmeyanov, Docklady Akad. Nauk SSSR., 1967,172.107.

26. G.G. Sumner, H.P. Klug, and L.E. Alexander, Acta Cryst., 1964,17,732.

27. H.M. Powell and R.V.G. Evans, J.Chem.Soc., 1939,286.

28. L.F. Dahl, E.R. de Gil, and R.D. Feltham, J.Amer.Chem.Soc., 1969,91,1653.

29. R.H.B. Mais, P.G. Owsten, and D.T. Thompson, J.Chem.Soc.(A), 1967,1735.

30. L.F. Dahl and C.H. Wei, Inorg.Chem.,1963,2,328.

31. R.B. King, J.Amer.Chem.Soc., 1963,84,2460.

32. E.S. Bolton. R. Halvin, and G.R. Knox, J.Organometallic Chem., 1969,18,153.

33.a E.W. Abel and F.G.A. Stone, Quart.Rev., 1969,23,325.

b E.W. Abel, Quart.Rev., 1963,17,133.

34. S.D. Ibekwe, personal communication.

35. A.D. Westland, J.Chem.Soc., 1965,3060.

36. F.G. Mann and D. Purdie, J.Chem.Soc., 1935,1549.

37. G.E. Coates and C. Parkin, J.Chem.Soc.,1963,421.

38. E. Samuel, Bull.Soc.chim.France, 1966,3548.

39. S.A. Giddings, Inorg.Chem., 1964,3,684.

40. F.R. Hartley, J.Organometallic Chem., 1970,21,227.

41. H. Köpf and M. Schmidt, J.Organometallic Chem., 1965,4,426.

42. R.B. King and C.A. Eggers, Inorg.Chem.,1968,7,340.

43. M.G. Harriss, M.L.H. Green, and W.E. Lindsall, J.Chem.Soc.(A), 1969,1453.

44. R. Ralea, C.Ungurenasu, and S. Cikoharu, Rev.Roumanie Chim., 1967,12,861.

45. H. Köpf, B. Block, and M. Schmidt, Chem.Ber. 1968,101,272.

46. H. Köpf and B. Block, Z. Naturforsch., 1968,23b,1534.

47. G.A. Razuvaev and V.N. Latyaeva, Organometallic Chem.Rev., 1967,2,349.

48. R.S.P. Coutts, J.R. Surtees, J.M. Swan, and P.C. Wailes, Austral.J.Chem., 1966,19,1377.

49. H. Köpf and M Schmidt, Angew.Chem.Internat.Edn., 1965,4,953.

50. H. Köpf and M. Schmidt, Z.anarg.Chem., 1965,340,139.

51. H.C. Beachell and S.A. Butter, Inorg.Chem., 1965,4,1133.

52. A.N. Nesmeyanov, E.I. Fedin, O.V. Nogina, N.S. Kochetkova, V.A. Dubovitsky, and P.V. Petrovsky, Tetrahedron, 1966, Suppl. 8, Part II, P.389.

53. J.A. Waters and G.A. Mortimer, J.Organometallic Chem., 1970,22,417.

54. F. Feher, B. Degan, and B. Söhngen, Angew.Chem. Internat.Edn., 1968,7,301.

55. J.C.W. Chien, J.Phys.Chem., 1963,67,2477.

56. C.J. Ballhausen and J.P. Dahl, Acta Chem.Scand. 1961,15,1333.

57. M. Gerlock and R. Mason, J.Chem.Soc., 1965,296.

58. J.R. Knox and C.K. Prout, Acta Cryst.B, 1969,25,2013.

59. J.R. Knox and C.K. Prout, Acta Cryst.B, 1969,25,2482.

60. N.W. Alcock, J.Chem.Soc.(A), 1967,2001.

61. E.F. Epstein and I. Bernal, Chem.Comm., 1970,410.

62. G.R. Davies and B.T. Kilbourn, to be published.

63. E.W. Abel and G.V. Hutson, J.Inorg.Nuclear Chem., 1969,31,3333.

64. G. Bouquet and M. Bigorgne, Bull.Soc.chim.France, 1962,433.

65. H.L. Nigam, R.S. Nyholm, and M.H.B. Stiddard, J.Chem.Soc., 1960,1803.

66. P.S. Braterman, J.Chem.Soc.(A), 1968,2907.

67. F.A. Cotton and C. Kraihanzel, J.Amer.Chem.Soc., 1962,84,4432.

68. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, 1966,2nd Edition, p.103.

69. A.L. Allred and E.G. Rochow, J.Inorg.Nuclear Chem., 1958,5,264.

70. H.C.E. Mannerskantz and G. Wilkinson, J.Chem.Soc., 1962,4454.

71. G.R. Davies, R.H.B. Mais, P.G. Owston, and D.T. Thompson, J.Chem.Soc.(A), 1968,1251.

72. L.F. Dahl and C.H. Wei, Acta Cryst., 1963,16,611.

73. D.M. Adams and J.B. Cornell, J.Chem.Soc.(A), 1968,1299.

74. S.F. Watkins, J.Chem.Soc.(A), 1969,1552.

75. J.T. Thomas, J.H. Robertson, and E.G. Cox, Acta Cryst., 1958,11,599.

76. M.P. Johnson and D.F. Shriver, J.Amer.Chem.Soc., 1966,88,301.

77. H. Brumner, P.C. Wailes, and H.D. Kaesz in "Abstacts of the Proceedings of the 2nd International Symposium on Organometallic Chemistry" Madison, Wisconsin, 1965, p.40.

78. B. Deubzer and H.D. Kaesz, J.Amer.Chem.Soc., 1968,90,3276.

79. D.J. Cook, J.L. Dawes, and R.D.W. Kemmett, J.Chem.Soc.(A), 1967,1547.

80. I.M. Nowell and D.R. Russell, Chem.Comm., 1967,819.

81. G.M. Sheldrick and R.N.F. Simpson, J.Chem.Soc.(A), 1968,1005.

82. A.A. Hock and O.S. Mills, Acta Cryst. 1961,14,139.

83. J.C. Katz and D.G. Pedrotty, Organometallic Chem.Rev., 1969,4,479.

84. A.B.P. Lever, "Inorganic Electronic Spectroscopy" Elsevier, 1968, p.9.

85. D.T. Thompson and R. Jackson, personal communication.

86. A.N. Nesmeyanov, A.I. Gusev, A.A. Pasynskii, K.N. Anisimov, N.E. Kolobova, and Y.T. Struchkov, Chem.Comm., 1968,1365.

87. L.F. Dahl and D.L. Wampler, Acta Cryst. 1962,15,903.

88.a B.W. Cook, R.G.J. Miller, and P.F. Todd, J.Organometallic Chem., 1969,19,421.

b P.F. Todd, personal communication.

89. J.H. Van Der Hende and W.C. Baird, J.Amer.Chem.Soc., 1963,85,1009.

90. N.C. Baenziger, H.L. Haight, and J.R. Doyle, Inorg.Chem., 1964,3,1535.

91. N.C. Baenziger, G.F. Richards, and J.R. Doyle, Inorg.Chem., 1964,3,1529.

92. V. Baran, Inorg.Nuclear Chem.Letters, 1970,6,375.

93. P.M. Druce, B.M. Kingston, M.F. Lappert, R.C. Srivastana, M.J. Frazer, and W.E. Newton, J.Chem.Soc(A), 1969,2814, and refs. therein.

94. D.C. Bradley and P.A. Hammersley, J.Chem.Soc.(A), 1967,1894.

95.a A.A. Chalmers, J. Lewis, and R. Whyman, J.Chem.Soc.(A), 1967,1817, and refs. therein.

b L.H. Jones, Spectrochim. Acta, 1963,19,329.

96. D.M. Adams, "Metal-Ligand and Related Vibrations" Arnold, London, 1967.

97. P.L. Goggin, R.J. Goodfellow, D.L. Sales, J. Stokes, and P. Woodward, Chem.Comm., 1968,31.

98. D.P. Tate, J.M. Augl, W.M. Ritchey, B.L. Ross, and J.G. Grasselli, J.Amer.Chem.Soc. 1966,86,3261.

99. T.A. Manuel and F.G.A. Stone, Chem. and Ind., 1960,231.

100. D.M. Adams and J.B. Cornell, J.Chem.Soc.(A), 1967,884.

101. D.M. Adams and P.J. Lock, J.Chem.Soc.(A), 1967,620.

102. T. Boschi, B. Crociani, L. Toniolo, and U. Belluco, Inorg.Chem., 1970,9,532.

103. K.K. Joshi, British Patent, applied for/1968.

104. D.A. Dundell, P.L. Goggin, R.J. Goodfellow, M.G. Norton, and J.G. Smith, J.Chem.Soc.(A), 1970,545, and refs. therein.

105. E.W. Abel and C.R. Jenkins, J.Organometallic Chem., 1968,14,285.

106.a E.W. Abel, B.C. Crosse, and D.B. Brady, J.Amer.Chem.Soc., 1965,87,4397.

b E.W. Abel and B.C. Crosse, J.Chem.Soc.(A), 1966,1141.

107. R.B. King and N. Welcman, Inorg.Chem., 1969,8,2540.

108. E.W. Abel and B.C. Crosse, Organometallic Chem.Rev., 1967,2,443.

109. J.R. Holden and N.C. Baenziger, Acta Cryst. 1956,9,194.

110. R.A. Walton, Spectrochim.Acta, 1965,21,1795.

111. W. Kitching, C.J. Moore, and D. Doddrell, Inorg.Chem., 1970,9,541.

112. A.J. Chalk and J.F. Harrod, J.Amer.Chem.Soc., 1965,87,1133.

113. O. Kahn and M. Bigorgne, Compt.rend., 1968,266C,792.

114. B.J. Aylett and J.M. Campbell, J.ChemSoc(A),1969,1910.

115. S.F.A. Kettle and I.A. Khan, Proc.Chem.Soc., 1969,82.

116. D.J. Patmore and W.A.G. Graham, Inorg.Chem., 1966,5,1405.

117. J.A.J. Thompson and W.A.G. Graham, Inorg.Chem., 1967,6,1365.

118.a N.I. Shuikin, I.F. Belskii, and I.E. Grusko, Zhur.obschei Khim., 1959,29,1882.

b M. Kratochvil and J. Frejka, Chem.listy, 1958,52,151

c B.J. Aylett, J.Inorg.Nuclear Chem., 1960,15,87.

119.a Y.L. Baay and A.G. MacDiarmid, Inorg.Chem., 1969,8,986.

b Y.L. Baay and A.G. MacDiarmid, Inorg.Nuclear Chem. Letters, 1967,5,159.

120. R.B. King, Transcripts of the New York Academy of Sciences, 1966,28,889.

121. R.B. King, K.H. Pannell, C.R. Bennett, and M. Ishaq, J.Organometallic Chem., 1969,19,327.

122. A.D. Berry, E.R. Corey, A.P. Hagen, A.G. MacDiarmid, F.E. Soalfield, B.B. Wayland, J.Amer.Chem.Soc., 1970,92,1941, and refs. therein.

123. D.J. Cardin and M.F. Lappert, Chem.Comm., 1966,506.

124. O.Vohler, Chem.Ber., 1958,91,1235.

125. W. Hewetson and H.R. Watson, J.Chem.Soc., 1962,1490.

126. E.V. Bell and G.M. Bennett, J.Chem.Soc., 1928,3189.

127. H. Reinhardt, D. Bianchi, and D. Mölle, Chem.Ber., 1957,90,1656.

128. G.Booth and J. Chatt, J.Chem.Soc.(A), 1966,634.

129. M.S. Kharasch, R.C. Seyler, and F.R. Mayo, J.Amer.Chem.Soc., 1938,60,882.

130. G.T. Morgan and W. Ledbury, J.Chem.Soc., 1922,121,2862.

131. G.M. Bennett, A.N. Masses, and F.S. Statham, J.Chem.Soc., 1930,1668.

132. J. Chatt, L.M. Vallarino, and L.M. Venanzi, J.Chem.Soc., 1957,2496.

133. R.G. Hayter and F.S. Humiec, J.Inorg.Nuclear Chem., 1964,26,807.

134. R.D. Gorsich, J.Amer.Chem.Soc., 1960,82,4211.

135. K. Andra, J.Organometallic Chem., 1968,11,567.

136. J.H. Teuben, H.J. De Liefde-Meijer, J.Organometallic Chem., 1969,17,87.

137. H. Köpf and M. Schmidt, J.Organometallic Chem., 1967,10,383.

138. I. Iwai and Y. Yura, Takamine Kenkyusho Nempo, 1958,10,30. (Chem. Abs., 1961,55,4400d)

139. A.D. Petrov, L.L. Shchukovskaya, and Y.P. Egerov, Doklady Akad.Nauk SSSR., 1953,93,293. (Chem. Abs., 1954,48,13616g).

140. K. Clauss and H. Bestian, Annalen, 1962,654,8.

141. L. Summers, R.H. Uloth, and A. Holmes, J.Amer.Chem.Soc., 1955,77,3604.

142. G. Booth and J. Chatt, J.Chem.Soc., 1965,3238.

143. J.A. Broomhead and F.P. Dwyer, Austral.J.Chem., 1961,14,250.

144. J. Chatt and B.L. Shaw, Chem. and Ind., 1959,675;

J.Chem.Soc., 1960,1718.

145. R.B. King, J.Organometallic Chem., 1967,8,139.

146. R.B. King and A. Fronzaglia, Inorg.Chem., 1966,5,1837.

147. D.P. Tate, W.R. Knipple, and J.M. Augl, Inorg.Chem., 1962,1,433.

148. L. Malatesta and C. Cariello, J.Chem.Soc., 1958,2323.

149. K. Yamamoto, Bull.Chem.Soc.Japan, 1954,27,501.

150. M.I. Bruce and F.G.A. Stone, J.Chem.Soc.(A), 1967,1238.

151. B.F.G. Johnson, R.D. Johnston, P.L. Josty, J. Lewis, and I.G. Williams, Nature, 1967,213,901.

152. K.K. Joshi, personal communication.

153. S.D. Robinson and G. Wilkinson, J.Chem.Soc.(A), 1966,300.

154.a T.S. Piper, F.A. Cotton, and G. Wilkinson, J.Inorg.Nuclear Chem., 1955,1,165.

b F.A. Cotton, A.D. Liehr, and G. Wilkinson, J.Inorg.Nuclear Chem., 1955,1,175.

155. E. Weiss, K. Stark, J.F. Lancaster, and H. Murdoch, Helv.Chim.Acta, 1963,27,288.

156. R.B. King in "Advances in Organometallic Chemistry" Eds. F.G.A. Stone and R. West, Academic Press, Vol. 2, 1964, p.157, and refs. therein.

157.a S.V. Dighe and M. Orchin, Inorg.Chem., 1962,1,965.

b G. Bor and L. Marko, Spectrochim.Acta, 1960,16,1106.

158.a A. Lee Smith, J.Chem.Phys., 1953,21,2001.

b M.C. Fabin, J.Amer.Chem.Soc., 1953,75,1788.

159. L.I. Zakharkin, Izvest.Akad.Nauk SSSR., Otdel Khim. Nauk 1960,2244. (Chem. Abs. 1961,55,14341c)

160. H.W. Sternberg, I. Wender, R.A. Friedel, and M. Orchin, J.Amer.Chem.Soc., 1953,75,2717.

161. A.G. MacDiarmid and A.P. Hagen, Inorg.Chem., 1967,6,686.